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UNIVERSITY. OF ALBERTA

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THE CRYSTAL STRUCTURE DETERMINATIONS OF WILKINSON'S CATALYST AND ITS DIOXYGEN DERIVATIVES

by

© PETER BLAIR DONALDSON

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

DEPARTMENT....CHEMISTRY.....

EDMONTON, ALBERTA

(SPRING, 1974)

THE UNIVERSITY OF ALBERTA

FACULTY OF GRADUATE STUDIES AND RESEARCH

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research, for acceptance, a thesis entitled ..The Crystal..... Structure Determinations of Wilkinson's Catalyst and its Dioxygen Derivatives..... submitted by ..Peter Blair Donaldson..... in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

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Abstract

A brief chemical introduction is given which includes short discussions of the principles of oxidative addition, the history of the solution studies performed on *tris*-triphenylphosphinechlororhodium(I) - known as Wilkinson's catalyst, and types of dioxygen coordination.

The dioxygen derivatives of the above complex and its iodo analogue were synthesized. The crystal and molecular structures of the red and orange modifications of the catalyst and its *bis* and *tris*-triphenylphosphine dioxygen derivatives were determined.

The *bis*-phosphine dioxygen complex crystallizes in the space group $P\bar{1}$ (a, 13.889(7); b, 13.678(6); c, 11.433(5) Å; α, 105.73(4); β, 115.74(3); γ, 100.97(4)°) with 1 molecule per unit cell (ρ_{obs}, 1.470; ρ_{calc}, 1.469 g-cm^{-3}). The model converged to a final R factor of 0.044. The complex is a dimeric species with dioxygen molecules bridging the rhodium atoms in a novel manner.

The *tris*-phosphine complex crystallizes in the space group Pbca with 8 molecules per unit cell (ρ_{obs}, 1.411; ρ_{calc}, 1.416 g-cm^{-3}). The axial parameters are: a, 24.817(4); b, 18.359(2); c, 23.200(4) Å. The refinement converged at R = 0.049. The molecule contains a π-bonded dioxygen ligand with additional hydrogen bonding being evident. A discussion of the dioxygen bonding in

both derivatives is included.

The orange allotrope of $RhCl(P(C_6H_5)_3)_3$ crystallizes in the space group $Pna2_1$ (a, 19.470(3); b, 12.689(2); c, 18.202(3) Å) with 4 molecules per unit cell (ρ_{obs}, 1.363; ρ_{calc}, 1.367 g-cm^{-3}). The refinement converged at a conventional R factor of 0.047. The complex has a square planar central geometry with a small approximately tetrahedral distortion.

The red modification of $RhCl(P(C_6H_5)_3)_3$ crystallizes in the space group $Pna2_1$ (a, 32.96(1); b, 12.271(2); c, 11.013 g-cm^{-3}) with 4 molecules per unit cell (ρ_{obs}, 1.382; ρ_{calc}, 1.379 g-cm^{-3}). The refinement converged at R = 0.042. The complex has a more distorted central geometry than the orange form. Variations in the rhodium-phosphorus and phosphorus-carbon bond lengths within the same species are discussed and comparisons drawn between the two forms of the catalyst and the two dioxygen derivatives.

Two very brief appendices are included and give explanations of computer programmes used and symbols not defined in the text.

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CHAPTER I

Chemical Introduction

Transition metal complexes are known to be very reactive in promoting chemical reactions and play an important role in the transport of molecular oxygen. One such complex, $RhCl(P(C_6H_5)_3)_3$ [1,2], acts as a homogeneous catalyst in a number of chemical reactions [3] and binds molecular oxygen. It was extensively studied when the research described in this thesis was initiated. The following points are important when considering homogeneous catalysis by this complex: (1) the general principles of oxidative addition, (2) the history of the solution studies of $RhCl(P(C_6H_5)_3)_3$ and (3) the types of dioxygen coordination in transition metal complexes. These topics will be briefly presented in this chemical introduction.

A number of publications have appeared dealing with transition metal complexes that react in a catalytic manner and these have been classified as proceeding by mechanisms such as oxidative addition [4,5,6], insertion [7], ligand exchange [8] and reactions with Lewis acids or bases [9]. Attempts have also been made to outline the fundamentals of catalysis more generally [10,11], however no scheme has been presented, except perhaps the 16 and

18 electron rule [12], which relates the different reaction types or permits mechanistic predictions.

Principles of Oxidative Addition

The term oxidative addition has been used to describe a large variety of reactions in which an increase in the oxidation number of the metal is accompanied by an increase in the metal coordination number. The oxidation number is designated following the accepted convention of assigning to the ligands in the complex the shared electron pairs which constitute the metal-ligand σ-bonds. A typical reaction of this type is the hydrogenation of Vaska's compound [13,14] depicted in equation 1.

$$Ir^{(I)}(CO)Cl(P(C_6H_5)_3)_2 + H_2 \rightarrow Ir^{(III)}(CO)Cl(P(C_6H_5)_3)_2H_2 \qquad (1)$$

The occurrence of oxidative addition reactions shows an inverse dependence of the preferred coordination number with the d-electron population of the transition metal. This trend illustrates the constraints of the 18 electron (or noble gas) rule where stable configurations of complexes are restricted to those in which the total number of valence electrons (comprising the transition metal d electrons and the σ-bonding electron pairs donated by the ligands) does not exceed 18. Other

stable configurations usually having 16 electrons are known as coordinatively unsaturated complexes. These unsaturated complexes undergo a large number of catalytic reactions and coordinative unsaturation is a prerequisite for catalysis and usually a prerequisite for a complex to be able to react by an oxidative addition mechanism. The closed shell configurations corresponding to 18 valence electrons tend to be particularly stable and widespread.

Oxidative addition of Vaska's compound could be represented as [12]

$$ML_4 + L_2 \underset{+2e}{\overset{-2e}{\rightleftharpoons}} ML_6 \qquad (2)$$

d^8 (16 electrons) $\quad$ d^6 (18 electrons)

however Vaska *et al.*, [15,16] have shown such a classification proceeding by a two electron step, to be unrealistic. They found that the concept of integral oxidation states for the metal did not agree with the gradual variation in the carbonyl stretching frequencies as ligands of varying electron accepting abilities (acidities) were coordinated. These frequencies varied from 1967 cm^{-1} in the parent d^8 complex, with an oxidation number of 1.0 to a final value of 2075 cm^{-1} for chlorine addition, iridium oxidation state 3.0. The

carbonyl stretching frequencies were used to assign relative oxidation states to the metal. It was found that the addition of ligands was easily reversible to a relative oxidation state of 2.24, stable but still reversible from 2.46 to 2.85 and stable irreversible from 2.85 to 3.0. The complex $RhCl(P(C_6H_5)_3)_3$ has no such convenient spectroscopic feature and structural studies are required to furnish similar information.

Oxidative addition reactions of these complexes should not be considered as integral donations of electrons from the metal to the incoming ligand, the coordination number being increased simultaneously, but rather as a gradual sharing of charge depending upon the electronegativity of the new ligand. Ligands accepting only small amounts of charge would not be expected to coordinate strongly or, if diatomic molecules, they would not be particularly perturbed by such donation. Conversely ligands such as Cl_2 accepting large amounts of charge from the metal would be highly perturbed by this charge addition, strongly bound and the original diatomic structure destroyed. Other evidence to support this includes the structural data on dioxygen derivatives of Vaska's compound [17,18,19] and its analogues [20], where it was found that the greater the perturbation of the dioxygen molecule (as indicated by the increase in the

oxygen-oxygen distance), the more irreversible was the oxygenation. $(O_2)Ir(CO)Cl(P(C_6H_5)_3)_2$ has an oxygen-oxygen distance of 1.30(3) Å compared to 1.51(3) Å in the iodo analogue. The first complex can be deoxygenated, whereas the second cannot. This trend was also reflected in the structure of the complex $(O_2)Ir((C_6H_5)_2 - PCH_2CH_2P(C_6H_5)_2)_2$ where the oxygen-oxygen distance was 1.63(2) Å and again the oxygenation was irreversible. Vaska and a number of other authors have studied the reactions of related iridium and other d^8 complexes with gaseous molecules. The various influences upon reactivity have been separated and studied as follows.

Vaska et al., [21] studied the role of the metal by substituting cobalt and rhodium for iridium in the complex $Ir(2=phos)_2X$, where 2=phos : $cis\text{-}(C_6H_5)_2PCH=CHP - (C_6H_5)_2$ and X : Cl^-, I^-, BF_4^-, $B(C_6H_5)_4^-$. Although a number of studies [15,22-24] have been carried out, comparisons had only been made between second and third row transition metal complexes where the usual reactivity order was third row > second row and by assumption also > first row. Vaska et al., found a reactivity order of Co > Ir > Rh. They also noticed that the enthalpies of activation were proportional to the electronic excitation energy of the three complexes and possibly [25,26] to their ligand field stabilization

energies. The initial structure of the complex was also found to be important as $CoCl(P(C_6H_5)_3)_3$, reportedly tetrahedral [27], was relatively inactive to hydrogenation and oxygenation, whereas the more planar rhodium analogue [138] is reported to be reactive [3]. Ibers *et al.*,[20,28] and Amma *et al.*,[29] concluded from structural data on similar complexes that the overlap between the ligand and substrate orbitals was less in rhodium than iridium complexes, owing to the higher energies of the rhodium d orbitals.

Vaska, Chen and Senoff [14] examined the role of the halide and found that the reaction rate was proportional to the basicity of the complex in the series $(O_2)IrA(Co)(P(C_6H_5)_3)_2$; A:F, NCO, $OClO_3$, Cl, I etc. In addition the free energy of activation increased with increasing energy of the electronic transition in four halo complexes. The calculated enthalpy changes for oxygenation were also similar to that for oxymyoglobin [30].

Vaska and Chen [31] compared the rates of oxygenation of $IrCl(CO)(PR_3)_2$ and found that the rate of formation and stability was directly proportional to the basicity of the phosphine ligand. Steric complications [32] were also apparent as *ortho* substituted groups did not undergo oxygenation whilst *meta* and *para* substituted analogues did. Other bulky ligands also appeared to

inhibit the reaction. These effects have been illustrated structurally as the more basic complex $(O_2)Ir(CO)Cl((C_6H_5)_2(C_2H_5)P)_2$ [33] had a longer oxygen-oxygen bond length (1.46(2) Å) than its less basic analogue $(O_2)Ir(CO)Cl(P(C_6H_5)_3)_2$, (1.30(3) Å).

Vaska *et al.*, [15,16] and others [34-36] studied the effect caused by changing the incoming covalent molecule and found that the chlorine-iridium-carbon angle varied considerably. They proposed that in keeping with the concept of non-integral metal oxidation states, the geometries could be interpreted as involving fractional coordination numbers of the metal as some structures were clearly intermediate between regular structural types. When the 'acidity' of the incoming molecule was varied, it was found that the greater the acidity, the less reversible and more rapid was the resulting reaction.

Perhaps a better method of comparing these complexes is as a series of compounds either having 16 or 18 electrons depending upon whether the complex is coordinatively unsaturated or saturated. These electrons should not be designated as being specifically associated with either the metal or ligand orbitals but rather as being located in a series of metal-ligand orbitals, the nature of which depend upon the basicity of the initial metal complex and the acidity of the

incoming ligand.

Solution Studies of $RhCl(P(C_6H_5)_3)_3$

The initial publications of Wilkinson *et al.*,[3] and Bennett and Longstaff [1] suggested that $RhCl(P(C_6H_5)_3)_3$ underwent an initial dissociation step with loss of triphenylphosphine upon dissolution. The research mentioned in this thesis was initiated when this was still the accepted viewpoint. If such dissociation did take place then the solution species would either have solvent coordinated to the metal or be coordinatively unsaturated with a minimum of 14 electrons in degassed solutions. In recent years a large amount of research has been directed towards the understanding of the nature of the solution species as it was thought to be highly relevant to the action of $RhCl(P(C_6H_5)_3)_3$ as a homogeneous solution catalyst. In addition if such solution behaviour was correct then there appeared to be inconsistencies between the ostensibly similar compound $Ir(CO)Cl(P(C_6H_5)_3)_2$ and $RhCl(P(C_6H_5)_3)_3$ and the rhodium complex would not react by an analogous oxidative addition mechanism.

Eaton and Stuart [37] studied the ^{31}P NMR of $RhCl(P(C_6H_5)_3)_3$ in $CDCl_3$ and found no peaks of significance associated with free triphenylphosphine. They did however find some evidence of triphenylphosphine oxide and when the concentration of the complex was lowered to 10^{-3} M,

some small peaks possibly representing free triphenylphosphine were observed. They concluded that the degree of triphenylphosphine dissociation was less than 5% in solutions with concentrations in excess of 10^{-2} M. In addition there was no evidence of halide dissociation. The coordinated triphenylphosphine *cis-trans* splitting was then studied and the activation energy for *cis-trans* isomerisation found to be ~6 kcal-mole^{-1}. The rate of this isomerisation was greater than the rate of ligand exchange. A simple dissociative mechanism was thus eliminated as the mechanism of isomerisation. They then concluded that although the intermediate could have been a tetrahedral isomer this was not confirmed and the intermolecular mechanism probably involved a structure similar to an ion pair intermediate with one of the triphenylphosphine ligands less strongly bound than the other two. Their study directly contradicted the simple dissociative mechanism predicted by Wilkinson *et al.*, in solutions of concentration greater than 10^{-2} M. These earlier conclusions were based upon osmometric studies so Eaton and Stuart repeated this work and confirmed that the molecular weight of the solution species was approximately 600, thus indicating a *bis*-phosphine complex. The inconsistency between the NMR and osmometric findings thus remained.

Augustine and Van Peppen [38] found that the dissociation of $RhCl(P(C_6H_5)_3)_3$ occurred readily in benzene but was completely inhibited by even small amounts of ethanol: their results again being based upon osmometric studies. They also noticed that the amount of oxygen reacting with the complex was quite solvent dependent and postulated the rather unusual species $[(O_2)RhCl(P(C_6H_5)_3)_2]_2O$ as a product. However the analytical results leading to this formulation are far from convincing. The isomerisation of olefins by $RhCl(P(C_6H_5)_3)_3$ was also found [39] to be most dependent upon the presence of oxygen and the solvent used.

Lehman, Shriver and Wharf [40] suggested that although the solutions used in the osmometric studies had all been stated to be degassed, some oxygen may have been present, causing a lowering of the apparent molecular weight. They rigorously excluded air from their experiments and initially added BF_3 to the solution. If free triphenylphosphine was present they should have obtained the complex $(C_6H_5)_3PBF_3$, however no such species was formed. Freezing point studies were then undertaken with the solvents being first distilled under nitrogen, degassed at high vacuum and transferred in a high vacuum line [41,42]. On four determinations in benzene ranging from 2.39×10^{-3} to 5.85×10^{-3} M, they obtained a molecular weight of

950 ± 40 *cf.* 925 for the parent complex. Using 1,2-dichloroethane the value was ~920 for a 3.22 x 10^{-2} M solution. A trace of oxygen was then admitted and the apparent molecular weight in both solutions dropped to *ca.* 600 (in agreement with the previous osmometric results). It thus appeared that these earlier results were incorrect and that the presence of oxygen was causing the lowering of the apparent molecular weight. This was supported by the appearance of triphenylphosphine oxide peaks in the ^{31}P NMR studies of Eaton and Stuart as this complex has been shown [43] to be a product from the reaction of similar homogeneous catalysts with oxygen. The ^{31}P NMR results were confirmed at similar concentrations by Shriver et al.

Arai and Halpern [44] then determined the equilibrium constant for dissociation spectrophotometrically in benzene (1.4(± .4) x 10^{-4} M at 25°C) and again supported the amended conclusions that in more concentrated solution (in excess of 10^{-2} M), dissociation was not extensive.

The nature of $RhCl(P(C_6H_5)_3)_3$ in benzene and chlorinated hydrocarbons under inert atmospheres thus appeared to be settled. As the hydrogenation reactions involving this complex included an initial interaction with hydrogen it was necessary to find out whether this reaction proceeded by a normal oxidative addition

mechanism or involved, as was apparently the case in the oxygenation reaction, expulsion of a triphenylphosphine upon coordination of the gaseous molecule.

Meakin, Jesson and Tolman [45] undertook a UV spectrophotometric study of $RhCl(P(C_6H_5)_3)_3$ with hydrogen in methylene chloride and observed that as the concentration of hydrogen was increased only one isosbestic point was obtained (360 mμ). This indicated the presence of only two chromophoric species in solution. From their additional ^{31}P and ^{1}H NMR studies they concluded that these species must correspond to the equilibrium:

$$H_2 + RhCl(P(C_6H_5)_3)_3 \rightleftarrows H_2RhCl(P(C_6H_5)_3)_3 \qquad (3)$$

This reaction could then be considered as proceeding by an oxidative addition mechanism. Tolman [12] has proposed a complete mechanism for the hydrogenation of a terminal olefin by $RhCl(P(C_6H_5)_3)_3$ with two paths arising from the possibility of coordinating hydrogen or olefin initially.

Molecular Oxygen Complexes

Molecular orbital theory has given an explanation for the biradical nature of the dioxygen molecule in its ground state [46] ($^3\Sigma$). Table 1 shows the molecular orbital configurations for various states of dioxygen. The excited state $^1\Delta O_2$ is diamagnetic and is located at 23.4 Kcal-mole^{-1} [47] above the groundstate. The other diamagnetic

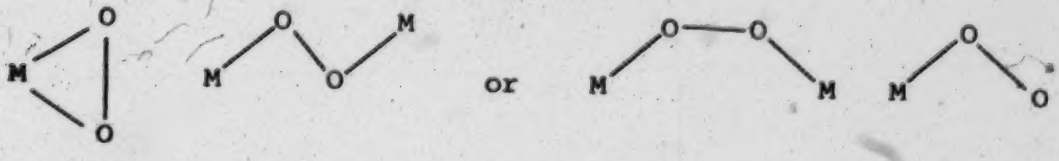
The other diamagnetic state $^1\Sigma$ with opposing spins requires even more energy (37.5 kcal-mole^{-1}). The superoxo ion (O_2^-) and the peroxo ion (O_2^{2-}) should be paramagnetic and diamagnetic respectively.

The geometries of the dioxygen molecular orbitals [48,49] are shown in Fig 1 and the oxygen-oxygen distances in O_2 ($^3\Sigma$), O_2^- and O_2^{2-} have been measured and are listed in Table 2. As a result coordinated dioxygen has tended to be classified on its oxygen-oxygen bond length alone and not by consideration of the geometry of the coordination between the metal and the dioxygen molecule. Species such as $(O_2)IrCl(CO)(P(C_6H_5)_3)_2$ and $(O_2)IrI(CO)(P(C_6H_5)_3)_2$ with oxygen-oxygen distances of 1.30(3) and 1.51(2) Å respectively, have thus been classified initially as containing either a superoxide or peroxide ion. They should however (as mentioned earlier) be viewed more realistically as involving differing degrees of charge transfer from the ligand to the metal and *vice versa* but not in an integral fashion. Unfortunately these bondlength classifications have been extensively used in the discussion of the bonding within a number of the following dioxygen cobalt complexes (see Table 4).

Compounds undergoing oxygenation have been of interest for some time as oxygen transport in biological

systems [50-52] and a number of autoxidation reactions [43-58] are thought to proceed by the formation of an initial oxygenated complex. The first example of a synthetic reversible dioxygen carrying complex was prepared in 1933 [59], when it was found that red-brown crystals of *bis*-salicylaldehyde ethylenediimine cobalt(II) darkened on exposure to air. It was five years before this darkening was attributed to the reaction with molecular oxygen [60]. Much research [47,61-63] has been directed into understanding the nature of this complex and other dioxygen species.

Definitive studies of the structures of dioxygen complexes suggest three major structural categories:



(I) (II) (III)

A large number of class (I) complexes have been prepared [47] some of which are represented in Table 3. The bonding in these complexes was first proposed by Griffith [64] and is discussed in later chapters. A number of cobalt complexes with class (II) structures are known, the more important mentioned in Table 4. These complexes have either a planar μ-superoxo dioxygen bridge, the compounds thus

being paramagnetic with oxygen-oxygen distances of 1.28 - 1.36 Å; or a non planar μ-peroxo bridge in diamagnetic species with large variations in the torsional angles and oxygen-oxygen distances when compared to H_2O_2. The μ-superoxo complexes can occur in either staggered or eclipsed conformations.

Class (111) complexes are postulated to contain a bent dioxygen-metal bond. This has been observed in the structure of [Co(bzacen)(O_2)]pyridine, bzacen = $((C_6H_5)C(O^-)CHC(CH_3)N(CH_2^-))_2$ [65] where the cobalt-dioxygen angle was 126° and the oxygen-oxygen distance 1.26(4) Å. A number of similar reversible oxygen carrying complexes have been studied [66-69] and along with oxycoboglobin [70] and oxyhemoglobin [71,72] have been postulated to contain similar structures.

A large amount of research has been directed towards understanding the mode of oxygen addition to hemoglobin and the matter still requires resolution. The bonding models of Griffith and Pauling [73] have both been found to represent structures in synthetic analogues. The bent dioxygen-metal bond may be the more favoured current view because of the similarities in the structure of [Co(bzacen)(O_2)] pyridine to that of vitamin B_{12} [74,75] and hemoglobin [76]. The pyridine geometry is analoguous to the histidine imidazole ring close to the metal

in the latter two proteins. Studies on a reversible iron(II) complex [77] suggest that the oxygenation of hemoglobin may be heavily influenced by the bulky peptide chains surrounding the active site. These may prevent the formation of a class(11) bridged complex and ensure the bent dioxygen bond.

Other dioxygen structures have been postulated for a variety of synthetic dioxygen complexes [78,79] with little or no structural justification.

The dioxygen complexes mentioned in this thesis may be viewed as belonging either purely to class (1) or as a mixture of class (1) and class (11) structural categories.

Table 1

Configurations of Various Dioxygen States

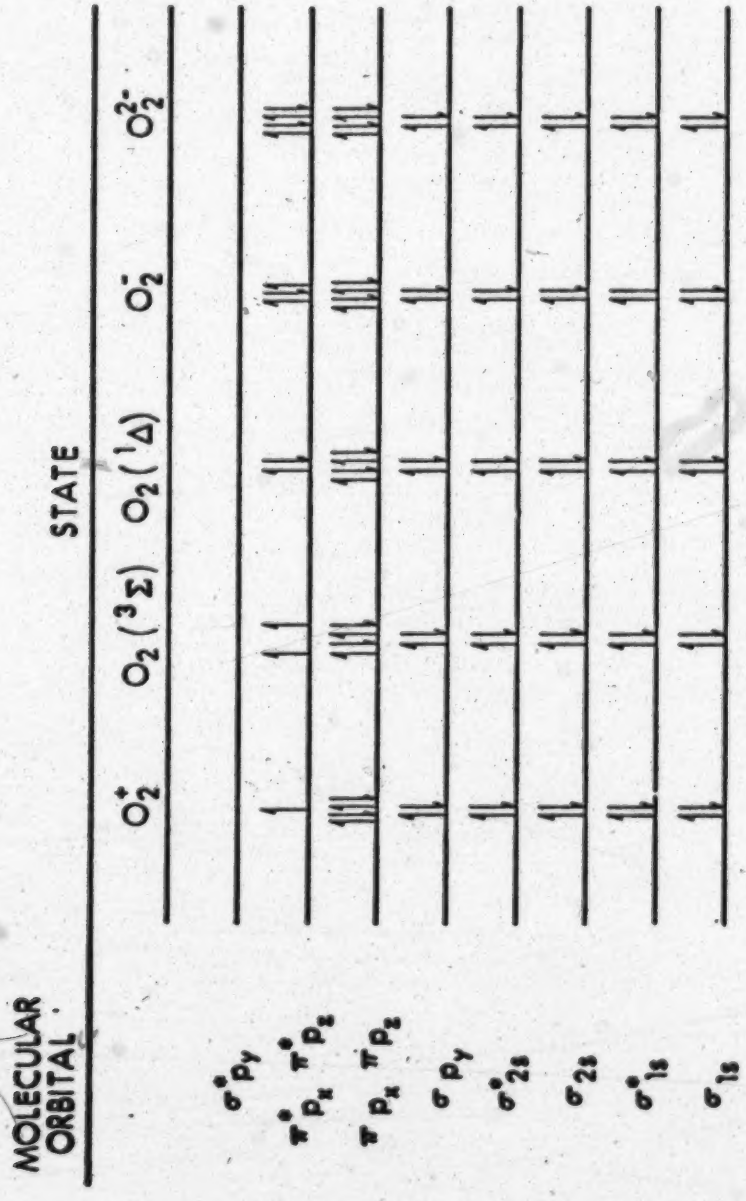


Fig. 1

Dioxygen Molecular Orbital Geometries

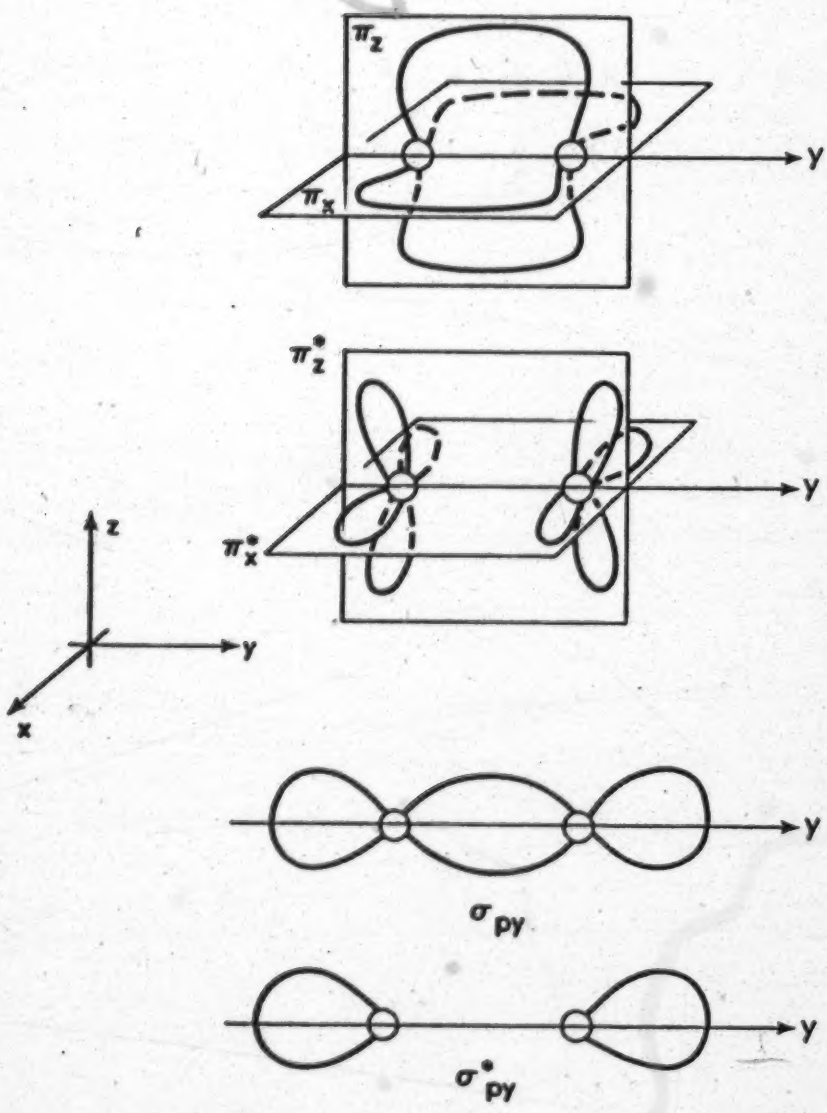


Table 2

A Selection of Simple Oxygen Containing Species

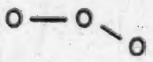
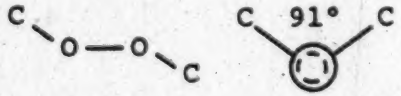
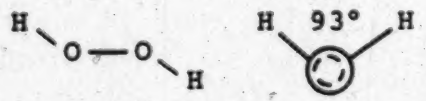
Species	Structure	Oxygen-Oxygen Distance (Å) and Comments	Reference
O_3		1.278(3)	80
O_2F_2		1.217(3) (non planar)	81
O_2^+	linear	1.1227(1)	80
O_2PtF_6	linear	1.17(2)	82
O_2	linear	1.2074(1)	80, 83
KO_2	linear	1.28(2)	80, 84
B-NaO_2	linear	1.33(6)	85, 86
$C_6H_5C(O)(O_2)C(O)C_6H_5$		1.46(2) (non planar)	87
H_2O_2		1.49(1) (non planar)	88
BaO_2	linear	1.49(4)	80, 89

Table 3

A Selection of Class (1) Dioxygen Complexes

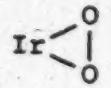
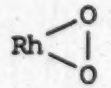
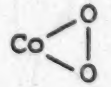
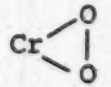
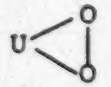
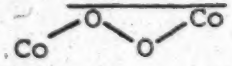
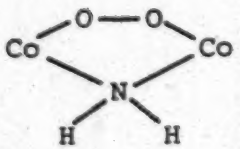
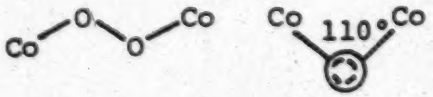
Complex	Structure	Oxygen-Oxygen Distance (Å)	Reference
$(O_2)IrX(CO)\alpha_2$			
X = Cℓ, α = $P(C_6H_5)_3$		1.30(3)	17
X = Br, α = $P(C_6H_5)_3$		1.36(4)	90
X = I, α = $P(C_6H_5)_3$		1.47(2), 1.51(2)	18, 10
X = Cℓ, α = $P(C_6H_5)_2(C_2H_5)$		1.46(2)	33
$[(O_2)Ir(2\text{-phos})_2]^+$		1.66(2)	20, 28
$[(O_2)Rh(2\text{-phos})_2]^+$		1.42(2)	28
$[(O_2)Co(2\text{=phos})_2]^+$		1.42(2)	29
$[(O_2)_4Cr]^{3-}$		1.41(4)	91
$[(O_2)_3UO]^{4-}$		1.51(6)	92

Table 4

A Selection of Class (11) Dioxygen Complexes

Complex	Structure	Oxygen-Oxygen Distance (Å) and comments	Reference
$[(NH_3)_5Co(O_2)Co(NH_3)_5]SO_4(HSO_3)_3$		1.31(3) paramagnetic, planar	93
$[(NH_3)_5Co(O_2)Co(NH_3)_5](NO_3)_5$	..	1.32(2) paramagnetic, planar	94
$[(Cn)_2Co(O_2)(NH_2)Co(Cn)_2](NO_3)_4$		1.36(3) paramagnetic, nearly planar	95
$[(NH_3)_4Co(O_2)(NH_2)Co(NH_3)_4](NO_3)_4$	..	1.32(1) paramagnetic, nearly planar	96
$[(Co(Safen))_2O_2](dmf)_2$		1.34(1) diamagnetic, non planar	97
$[(H_2O)Co(O_2)N_2F_2C_{16}H_{12}O_2-$ $Co(O_2)N_2F_2C_{16}H_{12}]_2$	..	1.31(3) non planar	98

(Table continued)

Table 4 continued

Complex		Structure	Oxygen-Oxygen Distance (Å) and comments	Reference
$[(NH_3)_5Co(O_2)(NH_3)_5](SO_4)_2$	..		1.47(1) diamagnetic, non planar	99
$[(NH_3)_5Co(O_2)Co(NH_3)_5](SCN)_4$	..		1.65(3) diamagnetic, planar	100

CHAPTER II

Synthetic Studies

Experimental

All reactions involving gaseous molecules were performed in sealed vessels. The solutions were degassed by freezing in a liquid nitrogen bath and pumping on the solid material. The gas to be reacted was then introduced and the solution allowed to warm up. This cycle was then repeated several times. Shriver [41] has discussed similar methods for handling air sensitive compounds.

Infrared spectra were obtained using a Perkin Elmer 421 spectrometer with a standard slit width and the ultraviolet studies were carried out with either a Cary 14 M or a Cary 15 recording spectrophotometer. The former machine was used with a Cary 1411 reflectance attachment and a $MgCO_3$ standard block for the diffuse reflectance spectra. In this study only a white light source was used as the UV lamps did not produce high enough outputs to give a spectrum.

Melting points were determined on a Koffler Hot Stage and during the slow heating of the sample, the microcrystalline structure was examined continuously by means of a microscope.

The micro- analyses (unless otherwise stated) were performed in this department by Mrs. D. Mahlow and Mrs. A. Dunn. The gas chromatography results were obtained by Mr. A. Clement of this department with a Sargent recorder and using an 8 ft. Linde molecular sieve at 82°C with a helium flow rate of 60 c.c.-min^{-1}. A Cahn Instruments Inc. Gouy Balance was used by Dr. D. Day who undertook the magnetic measurements. All mass spectroscopic studies were performed in this department with either an A.E.I. MS9 high resolution spectrometer or an A.E.I. MS12 medium resolution instrument. Both machines were operated at 70 ev.

Chemicals were either commercially available or prepared as mentioned below.

Methylene Chloride

Three different brands of this solvent were tried with the reactions proceeding only in the brand with the most stringent specifications (Fisher Scientific Co.). This solvent was initially redistilled but as no effect was observed on the reactions when the Fisher samples were used without further treatment, later studies did not include this precaution.

Rhodium Trichloride

This compound was purchased from the Fisher

Scientific Co. or from A.D. Mackay Ltd., the latter material being recrystallized before use.

Tris-triphenylphosphinechlororhodium (I) [$RhCl(P(C_6H_5)_3)_3$]

This complex was usually prepared by the method described in the literature [1,3] although one batch was obtained from Fluka AG, Switzerland. The crystals of the orange allotrope of this complex were produced by a variation of the usual method. A solution containing 1 g $RhCl_3 \cdot 3H_2O$ in 40 ml ethanol was added very slowly to a solution of 10 g triphenylphosphine in 100 ml ethanol, by diffusion through a filter paper over a number of days at 35°C. Microanalytical analysis (Calcd. C, 70.1; H, 4.9; Cl, 3.8; P, 10.0; Rh, 11.1; Found: C, 70.0; H, 4.9; Cl, 3.8; P, 10.1; Rh, 11.2) were performed by Pascher Microanalytisches Laboratorium, Bonn, Germany. These values were in excellent agreement. The melting point of the compound was 134-136°C.

Crystals of the red form of $RhCl(P(C_6H_5)_3)_3$ prepared for the structural study were obtained in an identical manner except that the triphenylphosphine ethanolic solution was added to the rhodium solution. Microanalytical analyses (Found: C, 70.6; H, 4.9) agreed with the literature values although the chlorine analyses proved unsatisfactory, owing to interference

from rhodium or phosphorus. The melting point (138-140°C) agreed with the literature value (138°C). The diffuse reflectance spectra of both forms is given in Fig. 2.

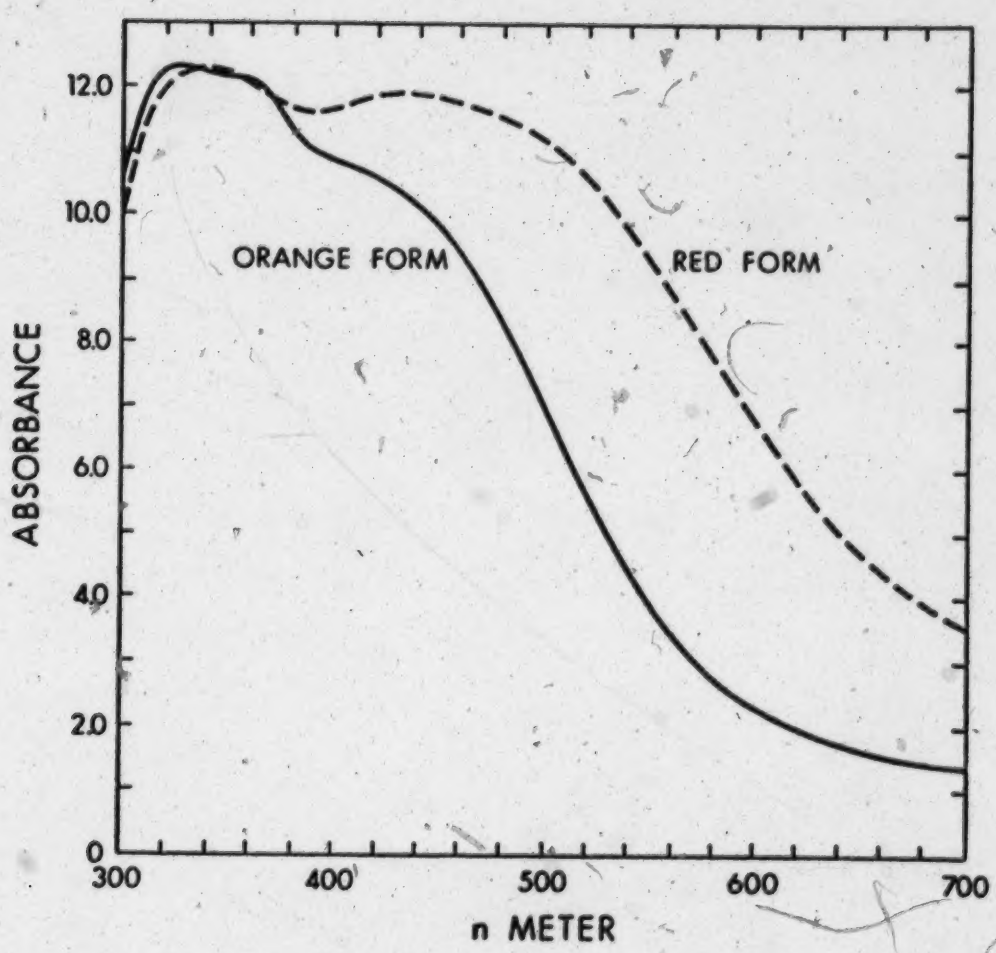
Dioxygen *bis*-triphenylphosphinechlororhodium dimer $[(O_2)RhCl(P(C_6H_5)_3)_2 \cdot CH_2Cl_2]_2$

When oxygen was bubbled through a solution containing 0.25 g $RhCl(P(C_6H_5)_3)_3$ in 15 ml methylene chloride and the solution slowly evaporated at 7°C for two days a ~50% yield of red-brown diamagnetic crystals was obtained. All measurements were made on this material which appeared to be homogeneous. Carbon and hydrogen analyses (Calcd: C, 57.0; H, 4.1; Found: C, 57.7; H, 4.2) were in reasonable agreement with the formulation but the chlorine analysis again proved difficult (Calcd: 13.6; Found: ~15).

Oxygen was positively identified in the gaseous thermal decomposition products by gas chromatography after heating the complex in vacuo to 20°C. The infrared spectrum of the solid residue showed an absorption (ν, 1120 cm^{-1}) consistent with the formation of complexed triphenylphosphine oxide [43,101]. The dimer undergoes a series of transformations during heating. The first visible transformation (80-85°C) appears to correspond to the complex dissolving in its own solvent of crystallisation. This was followed by loss of solvent (110-120°C)

Fig. 2

Reflectance Spectra of $RhCl(P(C_6H_5)_3)_3$

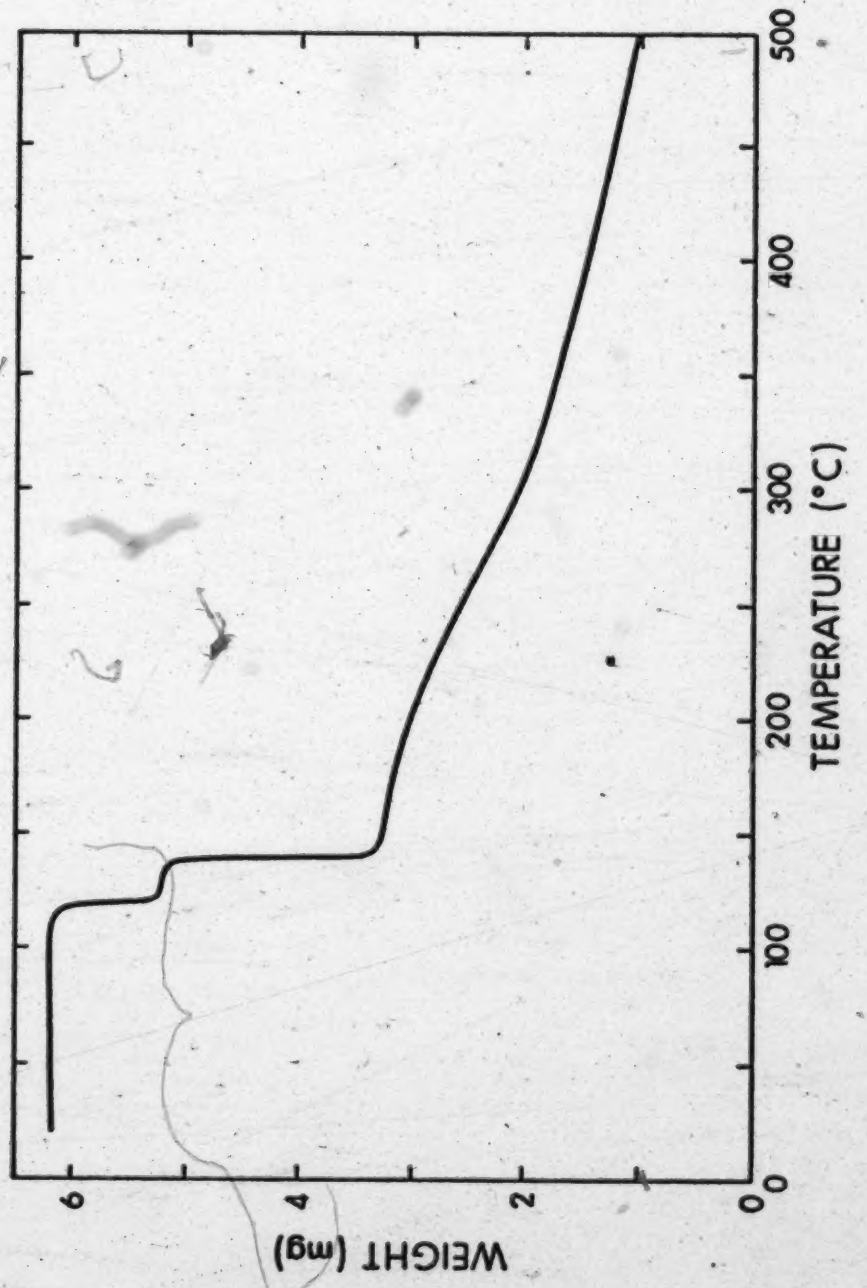


to give a glassy material which when heated to 134°C tends to explode violently. Thermal gravimetric analyses (carried out on a DuPont Thermalgravimetric Analyzer) over two days (Fig. 3) indicated that the complex loses methylene chloride and a triphenylphosphine below 130°C (gradual weight loss occurring above this temperature). At 500°C the mass of the residue corresponded to a mass of 150 per rhodium atom. Infrared and proton NMR spectra (Varian A60) verified the presence of free triphenylphosphine in the sublimate collected on the cool sides of the evacuated reaction tube. Mass spectrometric studies on the dimer (inlet temperature, 120°C) showed no parent peak or any recognisable peaks except triphenylphosphine, triphenylphosphine oxide and their degradation products. Identical behaviour was exhibited by all other compounds tested although a range of inlet temperatures was always tried.

$[(O_2)RhCl(P(C_6H_5)_3)_2 \cdot CH_2Cl_2]_2$ is extremely stable chemically, being inert to either strong acid or base and almost insoluble in all solvents tested. Recrystallisation was thus impossible, however no evidence of impurities was found. The complex does dissolve after prolonged exposure to pyridine and an orange crystalline product is formed. Analysis of this complex proved unsatisfactory. The infrared spectrum of the dimer (nujol

Fig. 3

$[(O_2)RhCl(P(C_6H_5)_3)_2 \cdot CH_2Cl_2]_2$ Thermal Weight Loss



mull, Fig. 4) showed the presence of an absorption at 845 cm^{-1} attributable to rhodium-dioxygen coordination [17].

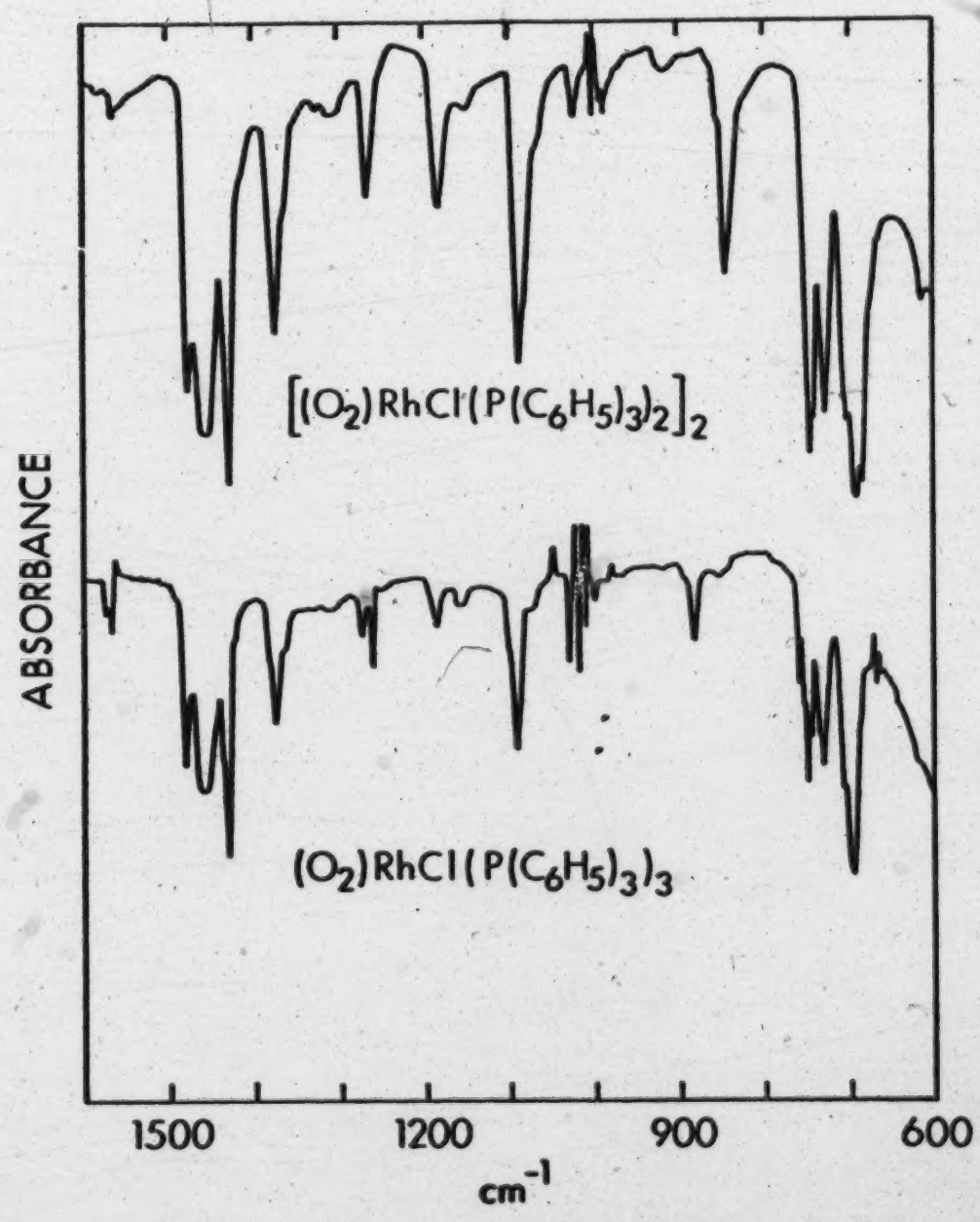
Dioxygen *tris*-triphenylphosphinechloro rhodium $[(O_2)RhCl(P(C_6H_5)_3)_3 \cdot 2CH_2Cl_2]$

Oxygen was bubbled through a solution, containing 0.5 g $RhCl(P(C_6H_5)_3)_3$ in 15 ml methylene chloride, for two minutes. After slow evaporation for 2 days at 7°C, yellow crystals of the complex (always accompanied by the dimer) were filtered off and washed with cyclohexane. The complex may also be produced by adding 0.25 g triphenylphosphine to 0.25 g $RhCl(P(C_6H_5)_3)_3$ and repeating the above procedure. Handpicked crystals were used in all subsequent tests.

Microanalytical analyses (Calcd: C, 59.7; H, 4.4; Found: C, 59.3; H, 4.4) were in reasonable agreement with the formulation although the chlorine analysis proved difficult. The compound melted at 82-84°C and decomposed at 126-128°C. The infrared spectrum (nujol mull) (Fig. 4) showed an absorption at 880 cm^{-1} assigned to the coordinated dioxygen. Similar studies on the products after heating to 200°C in vacuo indicated the presence of triphenylphosphine oxide in the solid residue. Oxygen was identified in the gaseous products by gas chromatography. Confirmation of the solid state formulation is contained in Chapter IV. Attempts to

Fig. 4

Infrared Spectra of Dioxygen Derivatives.



identify the *tris*-phosphine dioxygen complex in solution by the appearance of isosbestic points in the UV spectra were unsuccessful.

Tris-triphenylphosphineiodo rhodium (I) $[RhI(P(C_6H_5)_3)_3]$

RhI_3 (obtained by treating $RhCl_3$ in a water/ethanol solution with excess lithium iodide) was reacted with triphenylphosphine as described in the literature [3]. Microanalytical analyses (Calcd: C, 63.8; H, 4.4; I, 12.5; Found: C, 63.4; H, 4.6; I, 12.5) were in excellent agreement with the formulation and no evidence of chlorine was found. Melting point, 116-118°C, Lit., 118-120°C.

Dioxygen *bis*-triphenylphosphineiodo rhodium $[(O_2)RhI(P(C_6H_5)_3)_2]$

When 3.0 g of $RhI(P(C_6H_5)_3)_3$ in 20 ml methylene chloride was reacted with molecular oxygen for 2 minutes and the solution evaporated at 7°C for two days, black crystals were obtained in about 60% yield. Microanalytical analyses (Calcd: C, 54.9; H, 3.8; I, 16.1; Found: C, 54.2; H, 4.0; I, 16.2) were in good agreement with the formulation. Chlorine analysis failed to indicate the presence of methylene chloride although evidence of methylene chloride was found in the infrared spectrum (nujol mull), ν = 740 cm^{-1}. Strong absorptions

at 857 cm^{-1} with shoulders at 850 cm^{-1} and 838 cm^{-1} were assigned to coordinated dioxygen. Examination of fresh crystals under the microscope showed that a rapid breakdown of the crystals was occurring, possibly due to evolution of methylene chloride of crystallisation. This may explain the lack of chlorine in the analysis as this was performed after the infrared spectrum was obtained. The melting point was 166-168°C.

CHAPTER III

The Crystal and Molecular Structures of $[(O_2)RhCl(P(C_6H_5)_3)_2 \cdot CH_2Cl_2]_2$

Experimental

Brown crystals of $[(O_2)RhCl(P(C_6H_5)_3)_2 \cdot CH_2Cl_2]_2$ were obtained using the procedure outlined in Chapter II. These were examined under a microscope and found to be red-yellow pleochroic crystals, a large number of which were twinned. This twinning took the form of a diagonal missetting of the two crystal halves but was avoided by choosing one of a small number of crystals already cleaved in this direction.

Examination of preliminary Weissenberg and precession photographs indicated that the compound crystallized in the triclinic crystal system. The space group was therefore limited to P1 or $P\bar{1}$, the latter being verified by the successful solution and refinement of the structure.

Lattice parameters were found using the technique of centering the reflection in the diffractometer counter windows by adjusting the χ, ω and 2θ circles and checking at -2θ. Crude photographic lattice parameters were then subjected to a least squares refinement [102] to give the best agreement between the calculated and observed 2θ values. Lattice parameters were: a, 13.889(7); b, 13.678(6); c, 11.433(5) Å, α, 105.73(4); β, 115.74(3);

γ, 100.97(4)°). The density of the compound was measured by flotation in aqueous potassium iodide as 1.470 g-cm^{-3} which is in excellent agreement with the calculated density of 1.469 g-cm^{-3}.

The crystal was mounted on the end of a thin glass fibre so that the c* axis was coincident with the ϕ axis of the diffractometer. Intensity data were collected on a Picker manual 4-circle diffractometer using the coupled $\omega/2\theta$ scan method. Copper Kα X-radiation was employed and the diffractometer settings were calculated with the programme MIXG2 [103]. Intense peaks were carefully scanned to detect any twinning of the crystal and no evidence (such as splitting) was found. The diffractometer was equipped with a graphite crystal monochromator (002 reflecting plane) and a 2° take off angle was used. Each data point was scanned from 2θ - 1° to 2θ + 1° using a scan speed of 2° per minute. Background counts were estimated from a linear interpolation of 30 second stationary counts taken at the limits of the scan.

Data were only measured to 90° in 2θ as indicated by the preliminary photography. This rapid fall off in intensity was consistent with a relatively low degree of order in the crystals. A total of 2151 reflections were measured and of this number 1658 were found to be statistically reliable using the criterion $I \leq 3\sigma$. During the data collection 7 reflections were recollected at intervals

of 8 hours and changes in intensity noted. It was found that the crystal did decompose and that the relationship between the decomposition and time was logarithmic with an additional dependance upon the sin θ/λ value of the reflection. After data collection was completed all peaks with a count rate greater than 10^4 counts-sec^{-1} (i.e., more than the linear counting rate of the counter) were recollected at lower voltages and scaled into the data by comparison with other peaks of lower intensity recollected under the same conditions. The Miller indices of the crystal faces were identified as: 100, $\bar{1}00$, 010, $0\bar{1}0$, 001, $00\bar{1}$, $\bar{3}21$ and the dimensions of the crystal measured to allow an absorption correction to be made.

Reflection data were corrected for Lorentz [104] (L) and polarization (P) effects

$$L = 1 / \sin 2\theta$$

$$P = (\cos^2 2\theta_{\text{monochromator}} + \cos^2 2\theta) / 2$$

and the decomposition correction was applied. The absorption correction of the form

$$I = I_o e^{-\mu t}$$

where I_o = uncorrected intensity

μ = linear absorption coeff. (cm^{-1})

t = thickness (cm)

was made using the programme GONO9 [105] with $\mu = 72.13\ cm^{-1}$. The transmission factors varied from 0.809 to 0.633. Structure amplitudes ($|F_{rel}|$) and their standard deviations ($\sigma|F_{rel}|$) were then calculated with an uncertainty factor (p) of 0.03 from the equations: [106]

$$|F_{rel}| = \sqrt{I/LP}$$

$$\text{where } I = [CT - 0.5(t_c/t_b)(B_1 + B_2)]$$

$$\text{now} \qquad d|F_{rel}| = dI/2\sqrt{LPI}$$

$$\text{and} \qquad \frac{d|F_{rel}|}{|F_{rel}|} = \frac{1}{2}\frac{dI}{I}$$

making the approximation that $d|F_{rel}| = \sigma(|F_{rel}|)$ and $dI = \sigma(I)$ then

$$\sigma(|F_{rel}|) = \sigma(I)/2\sqrt{LPI}$$

where

$$\sigma(I) = [CT + 0.25(t_c/t_b)^2(B_1+B_2) + (pI)^2]^{1/2}$$

CT - total integrated peak count obtained in a scan time t_c, B_1 and B_2 being the background counts, each obtained in time t_b.

Solution of Structure and Refinement

The atomic coordinates of the heavy atoms, i.e., rhodium, chlorine and phosphorus were found by calculating a Patterson map [107] using the programme FORDAP [108]. Table 5 contains a listing of the prominent peaks in the Patterson map, together with their assignment and expected magnitude. Approximate coordinates consistent with the space group $P\bar{1}$ were obtained for these atoms.

From the results of the Patterson map it was apparent that the rhodium atoms were located approximately 3.5 Å apart, the molecule thus being dimeric. The other six atoms found were not situated in bridging positions so the molecule appeared to be bridged by either dioxygen or methylene chloride. The rhodium, chlorine and phosphorus atoms were included in the first refinement using SFLS5 [109]. The conventional R factor [110] (R_1) and R_2 (the weighted R factor) were 0.288 and 0.342 respectively, where

$$R_1 = \frac{\Sigma||F_o| - |F_c||}{\Sigma|F_o|} \quad \text{and} \quad R_2 = \left[\frac{\Sigma w(|F_o| - |F_c|)^2}{\Sigma w|F_o|^2}\right]^{1/2}$$

and $w = 1/\sigma^2(F)$

The remaining atoms in the unit cell were located as outlined in Table 6.

The carbon rings of the phenyl groups were constrained to D_{6h} symmetry, with carbon-carbon bond lengths

fixed at 1.392 Å, and refined as rigid bodies to minimize the number of parameters. The atomic scattering factors for the rhodium, chlorine, phosphorus and carbon atoms were derived from Cromer's coefficients [111] and included the real and imaginary terms for anomalous dispersion [112], for the rhodium, chlorine and phosphorus atoms. Hydrogen atoms were included at their calculated positions (carbon-hydrogen bond lengths, 1.0 Å) with isotropic temperature factors 10% larger than those of the carbon atoms to which they were attached. The hydrogen scattering factors were those of Mason and Robertson [113].

Initially (R_1 = 0.146) (Table 7), the nature of the methylene chloride electron density peaks indicated a disordered molecule, however methylene chloride was included as a single site model and further examination deferred until later in the refinement. The refinement (with $\Sigma w(|F_o| - |F_c|)^2$ being minimized) converged to give a conventional R factor of 0.055 for this model (cycle 10). At this point an electron density difference map was calculated and residual electron density around the position of the methylene chloride noted. Several models were tried to describe this disordered molecule. On the basis of minimal residual in electron density maps one model was chosen for the remainder of the refinement. This model used a single site (single occupancy) for the carbon atom and one chlorine atom (Cl4); the second chlorine atom

being resolved into two sites with variable occupancy factors (Cl2, 0.42(4); Cl3, 0.62(4)). The single site model for the carbon (C1) and chlorine (Cl4) atoms may be physically incorrect but the data do not permit resolution of the separate sites. The total model was then refined to convergence (shift/sigma, ~0.07) to give R_1, 0.044; R_2, 0.055.

Since the observed structure was so novel it was considered necessary to be absolutely certain that the bridging units were dioxygen molecules. When the scattering factors for nitrogen were used for these atoms the atomic thermal parameters assumed physically impossible values and R_1 increased to 0.051. Thus all evidence, both chemical (Chapter 2) and crystallographic (a Hamilton test [114] rejects the N_2 at better than the 0.005 confidence level) confirms the assignment of oxygen for these atoms.

A final electron density difference map was then calculated. The largest positive and negative peaks were 0.4 and -0.4 e-$\mathring{A}^{-3}$ respectively (c.f. carbon ~3 e-$\mathring{A}^{-3}$) and were located in the vicinity of the disordered methylene chloride molecule.

The atomic coordinates and their standard deviations of all atoms were then used to calculate interatomic bond lengths, angles and intra and intermolecular nonbonded contacts with their respective standard deviations, with the programme ORFFE II [115].

As the equivalent isotropic temperature factor of the chlorine atom (Cl1) was relatively large (4.17) a riding correction was applied to the rhodium-chlorine bond length. This compensates for the false shortening of this bond caused by the thermal motion description and its interpretation by the bond length programme. A similar correction was also applied to the rhodium-phosphorus bond lengths as a check. The thermal motion in these latter atoms was small so only slight changes were expected. This was indeed found to be the case. All atoms in these corrections were assumed to ride on a "stationary" rhodium atom.

Table 5

Assignment of Patterson Map Peaks

Peak Coordinates*			Relative Height (origin=999)	Assignment	Calculated Height	Calculated Coordinates (from Solution)		
u	v	w				u'	v'	w'
0.172,	-0.126,	0.124	228	$2x_a, 2y_a, 2z_a$	320	0.156,	-0.114,	0.132
-0.185,	0.116,	-0.136	236	$2\bar{x}_a, 2\bar{y}_a, 2\bar{z}_a$	320	-0.156,	0.114,	-0.132
-0.080,	-0.060,	-0.214	102	$x_a-x_b, y_a-y_b, z_a-z_b$	120	-0.083,	-0.060,	-0.250
-0.269,	0.050,	-0.370	108	$\bar{x}_a-x_b, \bar{y}_a-y_b, \bar{z}_a-z_b$	120	-0.273,	0.053,	-0.383
0.004,	0.160,	-0.006	158	$x_a-x_c, y_a-y_c, z_a-z_c$	107	0.032,	0.178,	0.022
-0.164,	0.292,	-0.110	123	$\bar{x}_a-x_c, \bar{y}_a-y_c, \bar{z}_a-z_c$	107	-0.162,	0.292,	-0.110
-0.164,	-0.038,	-0.006	106	$x_a-x_d, y_a-y_d, z_a-z_d$	107	-0.170,	-0.044,	-0.007
-0.353,	0.072,	-0.136	112	$x_a-x_d, y_a-y_d, z_a-z_d$	107	-0.360,	0.070,	-0.139

Space group $P\bar{1}$ solution a = Rh x, 0.078; $\bar{y}$, 0.060; z, 0.065

b = Cℓ1 x, 0.175, 0.005, 0.292

c = P1 x, 0.080, -0.226, 0.058

d = P2 x, 0.259, -0.009, 0.072

* These peaks with their combinations were the fourteen strongest peaks observed.

Table 6

Structure Solution Refinement Sequence

Refinement Cycle	Atoms used in Phasing	R_1	Atoms Located in Diff. Map.
1	Rh, Cℓ1, P1, P2,	0.288	O1, O2, C111-C116, C131-C136, C222-C226
2	Rh, Cℓ1, P1, P2, O1, O2 C111-C116, C131-C136, C222-C226	0.204	
3	..	0.186	C121-C126, C211-C216, C231-C236
4	Rh, Cℓ1, P1, P2, O1, O2 C111-C116, C121-C126, C131-C136, C211-C216, C221-C226, C231-C236	0.146	Methylene chloride located (included as a single site model)

Table 7

Refinement Sequence for Model

Refinement Cycle	Model Description	R_1	R_2
5	All atoms included, anomalous dispersion correction applied	0.112	0.136
6	..	0.091	0.116
7	Central atoms assigned anisotropic thermal parameters	0.077	0.090
8	..	0.071	0.083
9	Hydrogen atoms included	0.061	0.073
10	..	0.055	0.066
11	Methylene chloride represented as disordered model	0.049	0.060
12	..	0.046	0.057
13	..	0.044	0.055
14	Oxygen atoms replaced by nitrogen atoms	0.053	0.071
15	..	0.051	0.069

Results

Table 8 gives the observed ($|F_o|$) and calculated ($|F_c|$) structure amplitudes (electrons x 10). The atomic coordinates of all atoms are listed in Table 9 and the anisotropic temperature factors (U_{ij}) for the central atoms are given in Table 10. Interatomic distances (Table 11), interatomic angles (Table 12), intramolecular and intermolecular non bonded-contacts (Tables 13 and 14 respectively) are included with the standard deviations in parentheses.

A view [116] of the whole molecule is shown in Fig. 5. The central coordination geometry is represented in Fig. 6 and a view down the P1-O2' axis is given in Fig. 7.

Table 8

Observed and Calculated Structure Amplitudes (electrons x 10)

H	K	FOBS	FCAL	H	K	FOBS	FCAL	H	K	FOBS	FCAL	H	K	FOBS	FCAL	H	K	FOBS	FCAL
		KKL = 0		4	5	449	441	4	-7	341	355	1	-1	424	461	2	4	214	234
1	0	1409	1438	5	5	397	376	5	-7	493	492	2	-1	418	405	3	4	576	561
2	0	280	278	-6	6	412	405	6	-7	514	530	3	-1	390	410	4	4	272	295
3	0	986	916	-7	6	780	683	7	-7	333	336	4	-1	266	265	5	4	297	308
4	0	769	735	-6	6	382	365	9	-7	169	148	5	-1	492	517	6	4	498	479
5	0	1232	1196	-5	6	143	155	-6	-6	253	260	6	-1	578	605	-9	5	268	195
6	0	727	687	-3	6	718	722	-5	-6	519	556	8	-1	428	406	-8	5	954	947
7	0	267	245	-2	6	704	826	-4	-6	448	448	9	-1	366	399	-7	5	712	703
-10	1	399	395	-1	6	1159	1155	-3	-6	147	139	-7	0	449	489	-6	5	215	166
-9	1	326	326	0	6	333	323	-2	-6	293	289	-6	0	705	729	-5	5	366	362
-8	1	292	290	2	6	284	269	-1	-6	153	204	-5	0	700	678	-4	5	612	589
-7	1	378	378	3	6	417	420	0	-6	916	923	-4	0	433	458	-3	5	972	966
-6	1	984	629	4	6	494	488	1	-6	1306	1280	-3	0	725	648	-2	5	705	692
-5	1	859	838	5	6	568	569	2	-6	810	826	-2	0	361	375	-1	5	388	348
-3	1	461	473	-9	7	289	286	4	-6	286	272	-1	0	1446	1787	0	5	156	119
-2	1	341	324	-8	7	315	289	5	-6	242	270	0	0	1463	1476	2	5	714	705
-1	1	181	79	-7	7	798	791	6	-6	391	448	1	0	988	924	3	5	710	711
0	1	1873	1588	-6	7	658	636	7	-6	399	418	2	0	667	629	4	5	447	418
1	1	818	692	-5	7	550	638	8	-6	328	291	4	0	777	741	6	5	235	204
2	1	722	735	-3	7	506	480	-5	-5	536	536	5	0	946	974	-8	6	696	705
3	1	387	383	-2	7	874	869	-4	-5	598	611	6	0	886	796	-7	6	730	748
4	1	172	170	-1	7	696	719	-3	-5	498	485	8	0	157	170	-5	6	268	242
6	1	481	488	0	7	283	226	-1	-5	319	341	9	0	149	148	-4	6	425	408
7	1	418	482	2	7	138	132	0	-5	448	429	-10	1	224	199	-3	6	352	363
8	1	117	134	4	7	398	374	1	-5	1247	1257	-9	1	315	306	-2	6	580	570
-10	2	306	288	5	7	324	327	2	-5	1276	1257	-8	1	318	285	-1	6	721	703
-9	2	324	331	-9	8	493	484	3	-5	928	931	-7	1	236	247	2	6	370	362
-8	2	283	291	-7	8	955	968	4	-5	175	180	-6	1	956	957	3	6	961	982
-7	2	577	522	-6	8	644	630	7	-5	528	515	-5	1	991	987	4	6	727	709
-6	2	118	105	-5	8	470	462	8	-5	381	341	-4	1	427	421	5	6	223	248
-4	2	531	501	-4	8	294	314	-8	-4	212	223	-3	1	142	105	-10	7	147	126
-3	2	137	82	-2	8	374	362	-7	-4	345	360	-2	1	95	78	-9	7	668	621
-2	2	467	529	-1	8	133	111	-6	-4	603	644	-1	1	725	727	-7	7	703	702
-1	2	371	378	0	8	198	198	-5	-4	725	721	0	1	1036	1046	-6	7	498	491
0	2	258	257	2	8	282	143	-3	-4	358	377	1	1	684	677	-5	7	214	185
1	2	927	937	4	8	279	276	-2	-4	125	107	3	1	289	297	-3	7	368	369
2	2	799	799	-8	9	171	137	-1	-4	298	309	4	1	123	121	-2	7	903	494
3	2	579	611	-7	9	234	241	1	-4	828	819	5	1	568	569	-1	7	483	471
4	2	168	148	-6	9	368	343	3	-4	243	221	6	1	816	793	0	7	265	262
6	2	141	189	-5	9	286	258	4	-4	458	431	7	1	249	296	1	7	158	209
7	2	182	207	-4	9	345	335	5	-4	395	397	-10	2	288	275	3	7	497	507
-10	3	218	220	-2	9	224	252	6	-4	196	166	-8	2	582	535	4	7	532	551
-9	3	267	240	-1	9	197	174	7	-4	184	212	-7	2	188	253	-9	8	198	196
-8	3	418	373	0	9	168	156	8	-4	312	308	-6	2	341	335	-8	8	418	381
-7	3	489	483	2	9	136	128	9	-4	173	198	-5	2	648	637	-7	8	825	785
-6	3	186	168	-7	10	221	213	-9	-3	296	232	-4	2	533	559	-6	8	443	415
-4	3	111	83	-6	10	331	323	-7	-3	173	148	-3	2	774	715	-5	8	234	248
-3	3	1307	1313	-5	10	144	144	-6	-3	411	400	-1	2	142	125	-4	8	249	252
-2	3	1325	1256	-4	10	388	384	-5	-3	343	322	0	2	948	907	-2	8	159	173
-1	3	288	268	-3	10	178	195	-4	-3	188	194	1	2	403	412	-1	8	381	373
0	3	1718	1748	-2	10	229	222	-2	-3	221	217	2	2	248	249	0	8	374	384
1	3	1386	1342	-1	10	313	292	-1	-3	1012	994	3	2	281	265	1	8	181	201
2	3	443	474	0	10	242	235	0	-3	633	639	5	2	804	958	-7	9	504	487
3	3	230	229	KKL = 1		0000		1	-3	536	491	6	2	535	516	-6	9	227	226
4	3	187	185	2	-11	289	261	2	-3	1181	1141	7	2	166	177	-3	9	138	110
6	3	371	418	3	-11	589	576	4	-3	182	175	-10	3	299	158	-2	9	316	307
7	3	488	481	4	-11	471	467	5	-3	325	330	-8	3	592	602	-1	9	218	222
8	3	188	144	8	-11	238	261	6	-3	136	171	-7	3	183	171	-7	10	366	377
-8	4	386	426	0	-10	137	86	7	-3	695	687	-6	3	344	376	-4	10	248	265
-7	4	995	615	3	-10	272	298	8	-3	375	405	-5	3	683	611	-2	10	171	210
-6	4	134	144	4	-10	339	347	9	-3	193	182	-4	3	691	675	-1	10	222	204
-5	4	216	198	6	-10	262	260	-9	-2	211	212	-3	3	279	265	KKL = 2		0000	
-4	4	696	684	8	-9	488	481	-7	-2	288	289	-2	3	784	779	1	-11	145	142
-3	4	1122	1088	3	-9	478	481	-6	-2	484	378	-1	3	172	201	2	-11	580	521
-2	4	782	788	4	-9	515	528	-4	-2	384	415	0	3	628	632	3	-11	688	614
-1	4	418	397	7	-9	198	195	-3	-2	1881	1895	1	3	378	386	4	-11	178	144
0	4	713	730	-6	-8	295	211	-2	-2	281	264	2	3	189	198	-2	-10	374	326
1	4	1849	1853	0	-8	442	446	-1	-2	612	681	3	3	145	148	-1	-10	241	224
2	4	161	157	1	-8	576	574	0	-2	485	495	4	3	186	179	0	-10	147	160
4	4	478	480	2	-8	272	243	2	-2	1421	1401	5	3	511	568	2	-10	223	257
6	4	483	411	3	-8	389	481	3	-2	188	188	6	3	669	619	3	-10	591	609
7	4	323	295	6	-8	595	619	6	-2	391	392	7	3	489	478	-6	-9	319	341
-10	5	176	187	8	-8	477	482	8	-2	343	344	-10	4	182	158	-3	-9	186	124
-8	5	276	286	6	-8	368	330	7	-2	471	526	-9	4	237	214	-2	-9	334	342
-7	5	991	973	7	-8	224	167	8	-2	595	567	-8	4	687	680	-1	-9	536	543
-6	5	989	987	8	-8	225	188	9	-2	343	388	-7	4	388	345	0	-9	387	363
-4	5	388	382	-5	-7	214	225	-8	-1	142	131	-6	4	328	337	1	-9	248	226
-3	5	796	736	-4	-7	335	341	-7	-1	377	356	-5	4	351	388	2	-9	368	384
-2	5	878	845	-3	-7	946	982	-6	-1	384	413	-4	4	483	483	3	-9	487	444
-1	5	1636	1623	-1	-7	172	178	-5	-1	816	837	-3	4	825	831	5	-9	195	124
0	5	196	187	0	-7	288	192	-3	-1	1836	1811	-2	4	661	653	-8	-8	216	277
1	5	488	482	1	-7	698	788	-2	-1	947	968	-1	4	154	139	-4	-8	288	297
2	5	185	168	2	-7	391	383	-1	-1	1821	943	0	4	382	329	-3	-8	166	169
3	5	323	196	3	-7	188	189	0	-1	1836	1871	1	4	383	394	-2	-8	234	239

Table 8 (continued)

H	K	FOBS	FCAL	H	K	FOBS	FCAL	H	K	FOBS	FCAL	H	K	FOBS	FCAL	H	K	FOBS	FCAL
L = 20				-5	-2	386	385	-4	3	502	531	-3	-9	347	324	7	-3	505	536
-1	-8	436	432	-4	-2	1425	1427	-3	3	418	400	-2	-9	383	377	-9	-2	169	190
0	-8	224	244	-3	-2	788	772	-2	3	742	729	-1	-9	287	187	-8	-2	308	278
1	-8	393	393	-2	-2	1261	1174	0	3	343	336	1	-9	229	202	-7	-2	434	396
2	-8	336	331	0	-2	742	738	1	3	473	488	2	-9	190	222	-6	-2	384	377
3	-8	528	553	1	-2	1485	1457	3	3	262	251	3	-9	218	209	-4	-2	1297	1316
4	-8	265	267	2	-2	306	298	4	3	358	316	4	-9	148	124	-3	-2	174	128
6	-8	197	195	3	-2	237	225	5	3	412	388	7	-9	193	215	-2	-2	827	822
8	-8	418	396	4	-2	217	236	6	3	484	469	-6	-8	384	382	-1	-2	243	232
-8	-7	288	277	5	-2	315	326	-10	4	194	213	-5	-8	225	204	0	-2	388	397
-6	-7	433	442	6	-2	188	146	-9	4	193	227	-3	-8	447	459	1	-2	644	635
-5	-7	265	198	7	-2	582	590	-8	4	164	175	-2	-8	635	638	2	-2	574	583
-2	-7	539	549	8	-2	527	566	-7	4	219	198	-1	-8	416	409	3	-2	734	748
-1	-7	496	544	-8	-1	338	334	-6	4	546	527	2	-8	390	391	4	-2	252	281
0	-7	836	886	-7	-1	453	470	-5	4	338	334	3	-8	402	424	5	-2	248	262
1	-7	664	693	-6	-1	350	339	-4	4	263	274	4	-8	230	229	6	-2	429	475
3	-7	786	773	-5	-1	361	367	-3	4	157	181	5	-8	199	201	7	-2	991	628
4	-7	518	539	-4	-1	425	425	-1	4	234	258	7	-8	172	173	-10	-1	170	175
5	-7	446	442	-3	-1	1235	1196	0	4	520	545	-7	-7	229	199	-9	-1	296	275
6	-7	264	273	-1	-1	801	794	1	4	470	459	-6	-7	149	158	-8	-1	446	422
7	-7	420	389	0	-1	535	548	2	4	293	286	-5	-7	365	370	-7	-1	482	489
-7	-6	289	290	1	-1	499	506	4	4	288	267	-3	-7	490	511	-6	-1	273	264
-6	-6	250	237	3	-1	684	695	5	4	483	481	-2	-7	660	661	-5	-1	648	632
-2	-6	530	531	4	-1	556	557	6	4	331	337	-1	-7	994	982	-4	-1	1325	1348
-4	-6	721	751	5	-1	683	704	-10	5	292	308	0	-7	466	459	-2	-1	635	683
-3	-6	206	220	6	-1	305	308	-9	5	458	467	1	-7	198	178	-1	-1	652	637
-2	-6	737	742	7	-1	338	351	-8	5	526	541	2	-7	583	581	1	-1	448	486
0	-6	1202	1245	8	-1	448	452	-7	5	221	168	3	-7	526	516	2	-1	932	982
1	-6	897	904	-6	0	331	311	-6	5	677	628	4	-7	847	851	3	-1	973	972
2	-6	681	672	-7	0	747	715	-5	5	487	496	5	-7	522	541	4	-1	506	535
3	-6	305	292	-5	0	1268	1245	-4	5	648	648	6	-7	375	402	6	-1	269	293
4	-6	275	281	-4	0	605	611	-3	5	205	247	-8	-6	185	183	7	-1	232	212
5	-6	513	499	-3	0	1257	1327	-2	5	559	569	-6	-6	462	459	-11	0	229	235
6	-6	516	525	-2	0	231	213	0	5	281	264	-5	-6	629	633	-9	0	315	332
7	-6	654	647	-1	0	1584	1652	1	5	416	432	-3	-6	489	488	-8	0	458	497
8	-6	215	213	0	0	222	248	2	5	712	730	-2	-6	295	291	-7	0	658	681
-7	-5	147	169	1	0	195	186	3	5	484	510	-1	-6	510	514	-6	0	511	485
-6	-5	209	215	2	0	429	397	4	5	135	150	0	-6	433	434	-4	0	548	458
-5	-5	701	749	3	0	661	647	-10	6	336	354	1	-6	787	761	-3	0	308	316
-4	-5	1002	1035	4	0	799	761	-9	6	541	505	2	-6	635	601	-2	0	584	545
-3	-5	427	456	5	0	679	653	-8	6	857	812	4	-6	800	817	-1	0	882	866
-2	-5	204	196	6	0	486	480	-7	6	168	144	5	-6	528	578	0	0	823	809
-1	-5	981	994	8	0	312	288	-6	6	180	193	6	-6	757	776	1	0	190	196
0	-5	741	738	-11	1	427	445	-5	6	178	178	7	-6	678	686	2	0	307	296
1	-5	854	868	-10	1	227	241	-3	6	683	678	-6	-5	881	851	3	0	971	977
2	-5	292	276	-8	1	126	120	-2	6	1091	1092	-5	-5	950	918	4	0	710	727
3	-5	240	220	-7	1	978	988	-1	6	479	472	-4	-5	997	986	5	0	623	621
4	-5	172	168	-6	1	1054	1066	1	6	489	488	-2	-5	468	477	7	0	188	229
6	-5	234	220	-5	1	130	134	2	6	616	623	-1	-5	516	535	-11	1	428	361
8	-5	511	531	-4	1	317	270	3	6	735	717	0	-5	729	713	-9	1	248	239
7	-5	908	955	-3	1	676	626	4	6	336	309	1	-5	519	537	-8	1	457	449
8	-5	180	203	-2	1	1578	1532	-10	7	284	276	2	-5	579	582	-7	1	846	862
-8	-4	287	288	-1	1	1121	1080	-9	7	417	391	3	-5	387	405	-6	1	799	777
-7	-4	681	686	0	1	132	85	-8	7	772	751	5	-5	482	466	-5	1	252	289
-6	-4	220	210	1	1	111	81	-7	7	515	515	7	-5	386	381	-4	1	434	424
-5	-4	130	130	2	1	131	138	-6	7	237	249	-9	-4	298	342	-3	1	208	213
-4	-4	385	376	3	1	453	435	-5	7	131	169	-8	-4	273	276	-1	1	898	884
-3	-4	599	628	4	1	510	537	-3	7	141	121	-6	-4	286	317	0	1	1582	1647
-2	-4	872	871	5	1	660	677	-2	7	628	652	-5	-4	823	843	2	1	448	449
-1	-4	374	343	6	1	385	386	-1	7	501	457	-4	-4	496	478	3	1	739	714
0	-4	518	526	-11	2	436	443	1	7	185	198	-3	-4	277	288	4	1	520	509
1	-4	183	208	-10	2	437	413	2	7	235	221	-2	-4	129	161	5	1	410	404
2	-4	349	366	-9	2	305	290	3	7	483	502	-1	-4	383	345	-11	2	502	509
3	-4	542	507	-8	2	473	421	-8	8	390	391	0	-4	114	136	-10	2	242	248
4	-4	178	181	-7	2	624	647	-7	8	494	482	1	-4	297	288	-9	2	211	230
5	-4	248	211	-6	2	914	922	-6	8	248	246	2	-4	256	283	-8	2	278	267
6	-4	266	284	-5	2	781	784	-5	8	248	227	3	-4	386	395	-7	2	757	754
7	-4	482	486	-3	2	356	357	-4	8	283	263	5	-4	613	562	-6	2	779	770
-8	-3	183	176	-2	2	583	588	-2	9	457	477	6	-4	411	436	-5	2	741	695
-7	-3	330	340	-1	2	165	173	-1	9	295	288	8	-4	183	163	-4	2	336	330
-6	-3	409	400	0	2	351	355	-8	9	212	232	-5	-3	189	184	-3	2	333	327
-4	-3	912	929	1	2	434	444	-7	9	222	198	-4	-3	311	368	-2	2	869	871
-3	-3	563	543	2	2	169	162	-4	9	212	211	-1	-3	449	463	-1	2	753	745
-2	-3	328	338	3	2	299	289	-2	9	286	285	-5	-3	378	379	0	2	989	984
-1	-3	266	275	4	2	520	526	-1	9	335	341	-4	-3	498	399	2	2	272	269
1	-3	481	478	5	2	606	587	-4	10	266	229	-3	-3	128	117	3	2	398	336
2	-3	1117	1128	6	2	231	224	***L = 3*****				-2	-3	629	684	4	2	948	947
3	-3	263	223	-11	3	391	371	0	-11	239	229	-1	-3	958	958	5	2	145	126
6	-3	478	472	-10	3	286	294	1	-11	382	350	0	-3	837	834	6	2	191	181
7	-3	730	721	-9	3	239	217	2	-11	447	472	1	-3	788	780	-11	3	437	424
8	-3	347	356	-8	3	435	438	3	-11	384	344	2	-3	483	471	-10	3	199	193
-8	-2	366	385	-7	3	263	283	-9	-10	294	288	3	-3	288	317	-7	3	118	136
-7	-2	674	688	-6	3	859	817	2	-10	235	254	5	-3	241	278	-6	3	348	356
-6	-2	388	384	-5	3	811	802	3	-10	382	382	6	-3	602	649	-5	3	299	284

Table 8 (continued)

H	K	FOBS	FCAL	H	K	FOBS	FCAL	H	K	FOBS	FCAL	H	K	FOBS	FCAL	H	K	FOBS	FCAL
OOL = 3*****				-2	-8	378	362	4	-2	172	187	-5	5	662	647	-8	-4	336	298
-9	3	187	128	0	-8	180	191	5	-2	326	307	-4	5	291	280	-7	-4	187	147
-8	3	761	782	2	-8	288	291	6	-2	484	513	-3	5	434	432	-6	-4	984	942
-8	3	172	163	3	-8	388	388	-11	-1	203	268	-1	5	787	794	-2	-4	284	284
-1	3	178	183	4	-8	498	488	-10	-1	212	227	0	5	861	835	-1	-4	213	262
3	3	834	826	5	-8	233	216	-9	-1	402	332	2	5	336	325	0	-4	382	376
1	3	277	296	-7	-7	261	211	-8	-1	251	206	-10	6	443	438	1	-4	291	273
2	3	167	192	-6	-7	312	287	-5	-1	210	196	-9	6	781	781	2	-4	191	171
3	3	125	113	-5	-7	215	194	-4	-1	251	278	-8	6	514	469	3	-4	271	268
4	3	433	436	-4	-7	409	407	-3	-1	797	779	-6	6	414	396	5	-4	184	131
5	3	329	336	-3	-7	878	881	-2	-1	942	982	-5	6	760	781	-10	-3	293	304
-9	4	178	198	-2	-7	449	472	-1	-1	612	614	-4	6	729	738	-9	-3	203	198
-8	4	199	169	-1	-7	468	442	0	-1	617	611	-3	6	486	468	-8	-3	145	133
-7	4	161	136	0	-7	284	285	1	-1	1052	1048	-1	6	502	484	-6	-3	233	212
-6	4	389	351	2	-7	718	783	2	-1	999	1001	0	6	348	366	-5	-3	718	728
-4	4	189	206	3	-7	391	428	3	-1	953	966	1	6	192	178	-4	-3	148	158
-3	4	272	262	4	-7	741	717	4	-1	286	289	-9	7	428	441	-3	-3	199	231
-2	4	302	304	5	-7	289	246	5	-1	135	114	-8	7	500	513	-2	-3	184	144
-1	4	586	598	6	-7	185	185	6	-1	396	414	-7	7	338	368	-1	-3	471	485
0	4	758	788	7	-7	488	418	-10	0	867	862	-5	7	362	380	0	-3	983	989
1	4	385	388	-8	-6	482	384	-9	0	781	717	-4	7	498	475	1	-3	318	286
2	4	148	126	-7	-6	375	382	-8	0	417	407	-3	7	931	941	2	-3	287	223
4	4	284	248	-6	-6	477	482	-7	0	883	867	0	7	174	190	3	-3	378	348
-11	5	399	377	-4	-6	176	202	-6	0	229	232	-5	8	426	418	-10	-2	218	197
-10	5	311	297	-3	-6	385	376	-5	0	293	312	-4	8	223	239	-9	-2	383	385
-9	5	389	396	-2	-6	491	480	-4	0	816	822	-3	8	887	881	-7	-2	153	144
-8	5	287	184	-1	-6	582	523	-3	0	786	719	OOL = 5*****				-6	-2	749	739
-7	5	143	108	0	-6	382	391	-2	0	881	783	-3	-10	385	316	-4	-2	421	418
-6	5	239	228	1	-6	984	938	-1	0	721	736	-1	-10	145	117	-3	-2	477	483
-5	5	839	832	2	-6	131	119	0	0	471	448	0	-10	149	120	-2	-2	174	181
-4	5	727	698	3	-6	728	745	1	0	425	440	1	-10	346	338	-1	-2	746	729
-3	5	348	354	4	-6	753	730	2	0	634	661	2	-10	511	502	0	-2	1134	1149
-1	5	681	682	5	-6	693	694	3	0	845	832	-4	-9	272	278	1	-2	744	776
0	5	874	889	6	-6	886	873	4	0	388	371	-3	-9	189	177	2	-2	228	231
1	5	983	949	-9	-5	201	186	5	0	245	256	-1	-9	146	152	4	-2	228	258
2	5	468	438	-8	-5	228	195	-10	1	287	278	0	-9	238	227	5	-2	309	319
3	5	168	125	-7	-5	269	267	-9	1	368	388	1	-9	169	182	-11	-1	318	288
-10	6	491	496	-6	-5	636	656	-8	1	682	699	2	-9	248	262	-10	-1	282	149
-9	6	783	728	-5	-5	899	881	-7	1	685	671	3	-9	262	259	-9	-1	163	133
-8	6	492	509	-3	-5	135	110	-6	1	349	352	-4	-8	371	394	-8	-1	188	210
-7	6	188	206	-2	-5	281	241	-3	1	206	185	-3	-8	288	290	-6	-1	238	228
-5	6	479	482	-1	-5	332	337	-2	1	1030	1017	-2	-8	236	226	-5	-1	542	515
-4	6	736	748	0	-5	782	787	-1	1	844	848	-1	-8	144	113	-4	-1	399	396
-3	6	721	730	1	-5	984	914	0	1	120	67	1	-8	488	397	-3	-1	332	342
-2	6	438	411	3	-5	897	682	1	1	659	686	2	-8	711	782	-2	-1	467	429
0	6	488	492	4	-5	313	281	2	1	484	488	3	-8	617	554	0	-1	1098	1105
1	6	417	428	5	-5	983	848	3	1	178	216	5	-8	288	274	1	-1	774	768
2	6	848	879	6	-5	484	498	4	1	244	238	-8	-7	388	383	2	-1	477	458
-9	7	483	483	-9	-4	178	212	-11	2	278	234	-6	-7	521	504	3	-1	252	283
-8	7	686	613	-7	-4	267	278	-8	2	188	147	-3	-7	338	331	4	-1	258	283
-7	7	884	872	-6	-4	439	482	-6	2	768	782	-2	-7	385	323	-11	0	317	342
-6	7	311	281	-5	-4	665	688	-5	2	747	758	-1	-7	382	481	-10	0	452	443
-5	7	278	273	-4	-4	128	138	-4	2	819	482	0	-7	238	218	-9	0	632	628
-4	7	272	248	-3	-4	524	538	-2	2	886	882	1	-7	788	688	-8	0	692	738
-3	7	668	687	-2	-4	198	209	-1	2	698	712	2	-7	831	843	-7	0	467	452
-2	7	442	448	0	-4	129	111	0	2	194	167	3	-7	783	789	-5	0	578	531
-8	8	288	284	1	-4	478	486	1	2	448	427	4	-7	287	284	-4	0	885	822
-7	8	293	288	4	-4	381	313	3	2	178	192	-8	-6	411	386	-3	0	567	557
-6	8	234	219	5	-4	187	214	4	2	192	286	-7	-6	328	334	-2	0	784	778
-5	8	191	184	6	-4	288	217	-11	3	284	268	-6	-6	449	433	-1	0	284	282
-3	8	479	495	-10	-3	442	426	-8	3	134	88	-5	-6	133	117	0	0	625	625
-2	8	387	382	-9	-3	367	389	-7	3	348	343	-4	-6	132	142	1	0	515	497
0	8	187	185	-7	-3	193	191	-6	3	436	444	-3	-6	288	297	2	0	385	354
-7	9	368	338	-6	-3	278	238	-4	3	317	313	-2	-6	621	628	3	0	151	175
-6	9	221	282	-5	-3	993	890	-3	3	117	139	-1	-6	474	482	4	0	262	286
-3	9	496	479	-4	-3	481	379	-2	3	914	927	0	-6	917	904	-11	1	222	237
OOL = 4*****				-3	-3	284	265	-1	3	637	658	2	-6	498	498	-10	1	238	254
0	-11	237	228	-2	-3	182	167	0	3	276	248	3	-6	790	883	-9	1	273	273
1	-11	182	200	-1	-3	191	188	2	3	147	132	4	-6	342	389	-8	1	578	514
2	-11	388	376	0	-3	427	425	4	3	238	194	5	-6	548	548	-7	1	1022	1052
3	-11	177	178	1	-3	494	512	-9	4	198	189	-8	-5	388	296	-6	1	998	995
-3	-10	411	398	4	-3	271	295	-7	4	182	181	-7	-5	349	389	-5	1	243	243
-2	-10	191	204	5	-3	382	365	-5	4	363	384	-6	-5	738	735	-4	1	525	525
2	-10	277	264	6	-3	428	496	-4	4	888	894	-5	-5	383	389	-3	1	727	721
-4	-9	347	333	-10	-2	192	172	-2	4	794	718	-4	-5	345	357	-2	1	886	795
-3	-9	336	389	-9	-2	219	284	-1	4	998	987	-3	-5	271	294	-1	1	673	654
-2	-9	178	181	-8	-2	281	319	0	4	364	312	-1	-5	883	887	0	1	195	192
2	-9	283	230	-7	-2	177	183	1	4	146	186	0	-5	1116	1110	1	1	399	371
3	-9	898	878	-6	-2	734	736	-11	5	247	243	1	-5	421	382	2	1	278	298
4	-9	149	168	-5	-2	215	227	-10	5	288	232	2	-5	725	726	3	1	235	211
6	-9	248	214	-2	-2	982	975	-9	5	289	263	3	-5	482	496	4	1	384	312
-8	-8	211	196	0	-2	1181	1151	-8	5	278	285	4	-5	178	192	-9	2	138	91
-6	-8	481	483	1	-2	988	1000	-7	5	138	135	5	-5	443	487	-8	2	318	334
-5	-8	818	814	2	-2	871	888	-6	5	331	357	6	-5	188	188	-7	2	888	888

Table 8 (continued)

H	K	FOBS	FCAL	H	K	FOBS	FCAL	H	K	FOBS	FCAL	H	K	FOBS	FCAL	H	K	FOBS	FCAL
		***L =	5*****	3	-4	206	186	-3	2	226	212	-4	-3	179	189	-3	-6	248	227
-6	2	408	420	4	-6	205	178	-2	2	187	206	-3	-3	191	199	1	-4	467	483
-5	2	231	226	-9	-5	391	360	-1	2	172	201	-2	-3	303	260	-8	-5	269	316
-3	2	403	419	-7	-5	220	256	1	2	192	187	-1	-3	220	193	-7	-5	211	220
-2	2	371	373	-6	-5	623	602	-10	3	271	291	0	-3	425	495	-6	-5	278	268
-1	2	345	361	-5	-5	396	358	-8	3	346	321	2	-3	203	188	-4	-5	474	427
0	2	206	204	-3	-5	508	502	-7	3	683	678	3	-3	186	210	-3	-5	421	484
1	2	232	231	-2	-5	326	318	-6	3	283	279	-10	-2	250	263	-2	-5	332	300
-9	3	179	156	-1	-5	369	317	-4	3	349	392	-9	-2	197	169	-1	-5	279	237
-8	3	277	293	0	-5	359	344	-3	3	210	206	-7	-2	425	403	0	-5	249	227
-7	3	390	389	1	-5	281	253	-2	3	301	307	-6	-2	631	614	1	-5	163	195
-6	3	343	363	2	-5	443	438	-1	3	166	143	-5	-2	330	356	-7	-4	311	298
-4	3	324	307	-7	-4	285	263	1	3	150	175	-4	-2	312	341	-6	-4	185	195
-3	3	363	352	-6	-4	447	439	-10	4	192	178	-3	-2	344	321	-5	-4	227	193
-2	3	405	415	-5	-4	472	485	-9	4	189	173	-2	-2	198	212	-4	-4	185	118
-1	3	396	374	-3	-4	457	440	-8	4	364	379	-1	-2	318	308	-3	-4	230	98
1	3	190	214	-2	-4	484	392	-7	4	276	286	0	-2	481	417	-2	-4	162	177
3	3	155	156	-1	-4	401	396	-5	4	256	272	1	-2	243	241	-1	-4	268	250
-10	4	260	265	0	-4	286	300	-4	4	206	241	-10	-1	287	233	0	-4	299	331
-9	4	335	305	1	-4	152	119	-2	4	348	341	-9	-1	267	198	-9	-3	167	31
-7	4	467	489	2	-4	289	331	-1	4	415	392	-7	-1	309	364	-7	-3	183	197
-6	4	582	587	-10	-3	196	156	-8	5	343	346	-6	-1	710	690	-6	-3	278	282
-5	4	300	313	-9	-3	230	272	-7	5	699	687	-5	-1	415	389	-4	-3	197	166
-4	4	130	164	-7	-3	150	30	-6	5	293	271	-4	-1	127	65	-1	-3	382	311
-3	4	268	289	-6	-3	613	614	-5	5	171	234	-2	-1	162	168	-9	-2	282	276
-2	4	471	471	-5	-3	563	538	-2	5	345	382	-1	-1	437	424	-6	-2	338	315
-1	4	667	687	-3	-3	366	328	-8	6	276	240	0	-1	501	495	-4	-2	167	186
0	4	292	274	-2	-3	429	438	-7	6	560	561	1	-1	539	529	-2	-2	198	192
-10	5	447	445	-1	-3	328	348	-6	6	445	420	-10	0	526	559	-1	-2	502	478
-9	5	404	438	0	-3	384	412	-5	6	397	422	-9	0	290	233	0	-2	322	341
-8	5	154	135	2	-3	179	258	-4	6	339	354	-8	0	373	353	-9	-1	295	196
-7	5	451	461	-8	-2	164	157		***L =	7*****		-7	0	259	231	-7	-1	458	447
-6	5	472	489	-7	-2	214	177	-4	-9	319	330	-6	0	768	744	-6	-1	983	939
-5	5	288	198	-6	-2	644	613	-1	-9	188	165	-5	0	712	715	-5	-1	898	871
-2	5	131	157	-5	-2	650	597	0	-9	431	395	-4	0	371	366	-2	-1	297	291
-1	5	567	624	-3	-2	545	526	1	-7	198	198	-3	0	430	421	-1	-1	561	529
0	5	148	127	-2	-2	311	303	-5	-8	291	278	-1	0	233	216	0	-1	604	560
1	5	298	356	-1	-2	221	222	-4	-8	464	484	0	0	498	478	-7	0	306	309
-10	6	396	408	0	-2	333	371	-2	-8	234	247	1	0	616	602	-6	0	649	680
-9	6	499	513	1	-2	286	321	-1	-8	187	198	-10	1	550	537	-5	0	676	682
-8	6	167	172	-11	-1	184	187	0	-8	231	243	-9	1	367	395	-4	0	439	458
-7	6	417	415	-10	-1	242	223	1	-8	580	572	-8	1	408	441	-3	0	281	293
-5	6	486	476	-9	-1	322	314	2	-8	485	482	-6	1	511	481	-1	0	497	492
-4	6	271	283	-8	-1	301	309	-5	-7	486	483	-5	1	675	653	-6	1	241	278
-3	6	191	168	-6	-1	407	388	-4	-7	602	673	-4	1	449	449	-5	1	384	327
-1	6	381	367	-5	-1	698	677	-3	-7	509	512	-3	1	607	604	-4	1	426	454
-8	7	397	408	-4	-1	604	658	-1	-7	232	233	-2	1	488	442	-3	1	403	369
-7	7	218	279	-1	-1	762	758	0	-7	383	341	0	1	302	293	-2	1	222	236
-6	7	453	485	0	-1	688	692	1	-7	709	684	1	1	401	442	-7	2	171	178
-5	7	309	325	1	-1	451	479	2	-7	538	526	-9	2	364	383	-5	2	231	166
-4	7	343	331	-11	0	328	286	-8	-6	241	282	-8	2	437	421	-3	2	382	368
-3	7	389	389	-10	0	512	496	-7	-6	485	385	-6	2	391	378	-7	3	267	253
		***L =	6*****	-9	0	525	544	-5	-6	168	147	-5	2	322	342	-5	3	289	253
0	-10	241	248	-8	0	472	481	-4	-6	510	499	-2	2	262	257		***L =	9*****	
1	-10	540	517	-7	0	327	335	-3	-6	833	835	-1	2	190	184	-5	-6	487	448
-6	-9	318	317	-6	0	499	543	-2	-6	278	263	0	2	182	187	-4	-6	385	365
1	-9	218	235	-5	0	1011	1010	-1	-6	174	116	-9	3	189	187	-3	-6	201	214
3	-9	208	170	-4	0	867	859	1	-6	387	358	-8	3	217	220	-5	-5	496	423
-4	-8	352	330	-3	0	214	198	2	-6	572	590	-7	3	182	183	-4	-5	992	899
-3	-8	419	412	-2	0	226	258	-8	-5	299	246	-5	3	195	198	-3	-5	358	395
0	-8	356	356	-1	0	230	229	-7	-5	670	699	-3	3	221	237	-2	-5	201	240
1	-8	753	740	0	0	243	296	-6	-5	361	363	-2	3	342	309	-9	-4	222	173
2	-8	692	672	1	0	418	397	-4	-5	604	644	-9	4	148	143	-3	-4	188	163
4	-8	302	285	2	0	333	343	-3	-5	632	614	-8	4	272	270	-2	-4	197	280
-7	-7	255	271	3	0	390	398	-2	-5	283	270	-7	4	345	323	-8	-3	278	309
-5	-7	385	295	-11	1	328	316	-1	-5	184	185	-5	4	248	251	-3	-3	217	202
-4	-7	738	734	-10	1	302	293	0	-5	164	148	-4	4	148	177	-8	-2	216	192
-3	-7	648	648	-9	1	302	302	2	-5	416	433	-3	4	294	285	-7	-2	268	256
-2	-7	466	450	-8	1	675	703	-9	-4	285	168	-7	5	483	524	-6	-2	239	238
0	-7	325	314	-7	1	345	369	-7	-4	417	385	-6	5	288	180	-5	-2	288	284
1	-7	865	846	-6	1	516	520	-6	-4	387	486		***L =	0*****		-4	-2	291	245
2	-7	734	738	-5	1	590	573	-4	-4	382	375	-4	-8	177	172	-3	-2	314	303
3	-7	362	388	-4	1	280	264	-3	-4	268	263	-2	-8	173	189	-2	-2	363	396
4	-7	165	139	-3	1	218	236	-2	-4	321	302	-1	-8	188	164	-8	-1	263	237
-6	-6	295	225	-2	1	257	259	-1	-4	241	223	-8	-7	321	296	-7	-1	395	322
-7	-6	426	410	-1	1	389	400	0	-4	283	274	-5	-7	553	518	-6	-1	542	517
-6	-6	380	392	1	1	273	262	2	-4	382	388	-4	-7	316	330	-5	-1	295	296
-4	-6	388	389	2	1	192	201	3	-4	184	187	-2	-7	275	278	-3	-1	317	344
-3	-6	441	464	-9	2	235	288	-10	-3	268	268	0	-7	213	230	-7	0	364	365
-2	-6	578	585	-8	2	472	439	-7	-3	320	300	-6	-6	294	285	-6	0	491	494
-1	-6	227	259	-7	2	489	494	-6	-3	426	467	-5	-6	582	576	-5	0	493	462
1	-6	345	377	-5	2	195	220	-5	-3	245	264	-4	-6	864	899	-4	0	395	376
2	-6	588	604	-4	2	326	311												

Table 9

Atomic Coordinates and Isotropic Temperature Factors for the Unique Contents of the Unit Cell.

Atom	x	y	z	B *
Rh	0.09542(7)	-0.05735(7)	0.06606(9)	2.45
Cl1	0.1776(3)	0.0039(2)	0.3167(3)	4.17
P1	0.0670(3)	-0.2351(2)	0.0442(3)	2.95
P2	0.2648(3)	-0.0127(2)	0.0728(3)	3.03
O1	-0.0255(6)	-0.1164(5)	-0.1361(7)	2.67
O2	-0.0884(6)	-0.0928(5)	-0.0666(7)	2.86
C1	0.172(2)	0.255(2)	0.492(2)	10.33
Cl2	0.223(2)	0.377(1)	0.484(2)	8.7
Cl3	0.305(3)	0.367(1)	0.606(5)	20.3
Cl4	0.1238(8)	0.2598(5)	0.6050(8)	20.4

* These values are equivalent isotropic temperature factors corresponding to the anisotropic thermal parameters shown in Table 10

(Table continued)

Table 9 (continued)

(a) Phenyl Carbon Rigid Bodies

Name	x	y	z	B
C111	0.133(1)	-0.2670(8)	0.198(1)	3.1(3)
C112	0.0663(9)	-0.3343(6)	0.2282(9)	3.8(3)
C113	0.118(1)	-0.3600(6)	0.3448(7)	5.0(3)
C114	0.237(1)	-0.3183(8)	0.432(1)	4.5(3)
C115	0.3033(9)	-0.2510(6)	0.4019(9)	4.9(3)
C116	0.251(1)	-0.2253(6)	0.2853(7)	4.2(3)
D	4.210(4)	$x^{1\ddagger}$	0.1848(5)	
E	3.026(9)	$y^{1\ddagger}$	-0.2967(4)	
F	5.267(9)	$z^{1\ddagger}$	0.3151(5)	
C121	0.0960(7)	-0.3181(5)	-0.0827(8)	3.1(3)
C122	0.0727(6)	-0.2976(5)	-0.2031(9)	3.9(3)
C123	0.0996(7)	-0.3538(6)	-0.2989(6)	4.6(3)
C124	0.1498(7)	-0.4305(5)	-0.2742(8)	5.0(3)
C125	0.1731(6)	-0.4510(5)	-0.1538(9)	4.4(3)
C126	0.1462(7)	-0.3948(6)	-0.0581(6)	3.9(3)
D	2.712(4)	x^{1}	0.1229(4)	
E	1.647(5)	y^{1}	-0.3743(4)	
F	3.889(5)	z^{1}	-0.1785(5)	
C131	-0.0850(5)	-0.3020(7)	-0.0251(9)	2.8(2)
C132	-0.1318(7)	-0.2561(5)	0.0515(9)	4.1(3)
C133	-0.2434(8)	-0.3101(7)	0.0128(8)	5.4(3)
C134	-0.3083(5)	-0.4099(7)	-0.1026(9)	5.7(3)

(Table continued)

Table 9 (continued)

Name	x	y	z	B
C135	-0.2614(7)	-0.4557(5)	-0.1792(9)	5.9(3)
C136	-0.1498(8)	-0.4018(7)	-0.1405(8)	4.4(3)
D	0.680(4)	x^1	-0.1966(4)	
E	0.445(6)	y^1	-0.3559(4)	
F	0.198(6)	z^1	-0.0638(5)	
C211	0.3531(6)	0.1322(5)	0.1712(9)	3.1(3)
C212	0.4363(8)	0.1728(7)	0.1425(9)	4.4(3)
C213	0.5123(6)	0.2797(7)	0.2237(9)	5.2(3)
C214	0.5051(6)	0.3459(5)	0.3337(9)	5.0(3)
C215	0.4219(8)	0.3053(7)	0.3625(9)	5.2(3)
C216	0.3459(6)	0.1985(7)	0.2812(9)	3.9(3)
D	0.598(5)	x^1	0.4291(4)	
E	0.871(6)	y^1	0.2391(4)	
F	4.332(6)	z^1	0.2525(5)	
C221	0.241(1)	-0.0358(5)	-0.1031(9)	3.2(3)
C222	0.1490(9)	-0.0154(6)	-0.194(1)	4.4(3)
C223	0.1290(8)	-0.0268(6)	-0.328(1)	5.8(3)
C224	0.201(1)	-0.0584(5)	-0.3712(9)	6.3(4)
C225	0.2940(9)	-0.0788(6)	-0.281(1)	6.1(3)
C226	0.3140(8)	-0.0675(6)	-0.147(1)	4.5(3)
D	2.202(5)	x^1	0.2215(5)	
E	1.800(7)	y^1	-0.0471(4)	
F	3.215(8)	z^1	-0.2372(6)	

(Table continued)

Table 9 (continued)

Name	x	y	z	B
C231	0.3710(7)	-0.0724(7)	0.1519(7)	3.3(3)
C232	0.3685(7)	-0.1722(6)	0.0755(8)	4.2(3)
C233	0.4474(8)	-0.2165(5)	0.143(1)	6.0(3)
C234	0.5289(7)	-0.1610(7)	0.2865(7)	6.0(3)
C235	0.5314(7)	-0.0611(6)	0.3629(8)	5.4(3)
C236	0.4524(8)	-0.0168(5)	0.296(1)	3.9(3)
D	2.879(5)	x^1	0.4499(4)	
E	2.434(5)	y^1	-0.1167(4)	
F	5.514(5)	z^1	0.2192(6)	

† These values represent the coordinates of the ring center of gravity.

(Table continued)

Table 9 continued

(b) Phenyl Hydrogen Rigid Bodies

Name	x	y	z	B
H112	-0.019	-0.364	0.165	4.1
H113	0.070	-0.408	0.365	5.4
H114	0.274	-0.337	0.515	4.9
H115	0.388	-0.221	0.464	5.3
H116	0.299	-0.177	0.264	4.6
D	4.210			
E	3.026			
F	6.314			
H122	0.0371	-0.242	-0.221	4.3
H123	0.083	-0.339	-0.385	5.1
H124	0.169	-0.471	-0.343	5.5
H125	0.209	-0.506	-0.136	4.8
H126	0.163	-0.410	0.028	4.2
D	2.712			
E	1.647			
F	4.936			
H132	-0.085	-0.184	0.134	4.4
H133	-0.277	-0.277	0.068	5.9
H134	-0.388	-0.448	-0.130	6.3
H135	-0.308	-0.527	-0.262	6.5
H136	-0.116	-0.435	-0.196	4.8

(Table continued)

Table 9 (continued)

Name	x	y	z	B
D	0.680			
E	0.444			
F	1.245			
H212	0.441	0.125	0.063	4.8
H213	0.572	0.309	0.203	5.7
H214	0.560	0.423	0.392	5.5
H215	0.417	0.353	0.441	5.7
H216	0.286	0.169	0.302	4.3
D	0.598			
E	0.871			
F	5.380			
H222	0.097	0.007	-0.162	4.8
H223	0.062	-0.012	-0.392	6.3
H224	0.187	-0.067	-0.468	6.9
H225	0.346	-0.101	-0.312	6.7
H226	0.380	-0.082	-0.082	4.9
D	2.202			
E	1.800			
F	4.262			
H232	0.310	-0.212	-0.028	4.6
H233	0.446	-0.288	0.088	6.6
H234	0.586	-0.193	0.335	6.6

(Table continued)

Table 9 (continued)

Name	x	y	z	B
H235	0.590	-0.021	0.466	5.9
H236	0.454	0.055	0.350	4.3
D	2.879			
E	2.434			
F	6.561			

Table 10

Anisotropic Temperature Factors ($Å^2 \times 10^3$)

Atom Name	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Rh	33.4(7)	31.6(6)	31.0(7)	15.9(5)	16.6(5)	13.8(5)
P1	46(2)	35(2)	33(2)	20(2)	19(2)	15(2)
P2	38(2)	41(2)	35(2)	17(2)	16(2)	16(2)
Cℓ1	73(2)	52(2)	34(2)	29(2)	25(2)	17(2)
O1	33(5)	45(5)	31(5)	22(4)	16(4)	11(4)
O2	32(5)	34(5)	38(5)	19(4)	16(4)	19(4)
C1	180(20)	120(20)	70(10)	50(20)	70(20)	100(10)
Cℓ2	100(10)	120(10)	120(20)	46(8)	70(10)	37(8)
Cℓ3	240(30)	160(10)	450(50)	80(10)	250(30)	90(20)
Cℓ4	420(10)	129(5)	207(7)	21(6)	203(8)	22(5)

Table 11

Interatomic Distances

Atom 1	Atom 2	Distance (Å)	
Rh	P1	2.314(3)	2.316(3)*
Rh	P2	2.277(3)	2.281(3)*
Rh	Cl1	2.390(3)	2.402(3)*
Rh	O1	1.983(7)	
Rh	O2	2.198(7)	
Rh'	O1	2.778(7)	
Rh	O2'	2.069(7)	
P1	C111	1.815(7)	
P1	C121	1.829(7)	
P1	C131	1.829(7)	
P2	C211	1.833(7)	
P2	C221	1.821(8)	
P2	C231	1.832(7)	
O1	O2	1.44(1)	
Cl	Cl2	1.70(3)	
Cl	Cl3	1.80(3)	
Cl	Cl4	1.70(3)	

* Distance corrected for riding

Table 12

Selected Intramolecular Angles

Atom 1	Atom 2	Atom 3	Angle (°)
P1	Rh	P2	100.3(1)
P1	Rh	Cℓ1	90.6(1)
P1	Rh	O1	87.5(2)
P1	Rh	O2	92.5(2)
P1	Rh	O2'	169.4(2)
P2	Rh	Cℓ1	95.7(1)
P2	Rh	O1	106.2(3)
P2	Rh	O2	143.4(2)
P2	Rh	O2'	89.2(2)
Cℓ1	Rh	O1	158.0(3)
Cℓ1	Rh	O2	118.4(2)
Cℓ1	Rh	O2'	93.4(2)
O1	Rh	O2	39.9(3)
O1	Rh	O2'	85.2(3)
O2	Rh	O2'	76.9(3)
Rh	P1	C111	121.3(3)
Rh	P1	C121	115.5(3)
Rh	P1	C131	107.4(3)
Rh	P2	C211	114.5(3)
Rh	P2	C221	110.7(3)
Rh	P2	C231	120.6(3)
Cℓ2	C1	Cℓ3	47. (1)

(Table continued)

Table 12 (continued)

Atom 1	Atom 2	Atom 3	Angle (A°)
Cl2	C1	Cl4	116. (1)
Cl3	C1	Cl4	100 (1)
O1	O2	Rh'	103.4(5)
O1	O2	Rh	61.7(4)
Rh	O2	Rh'	103.0(3)

Table 13

Selected Intramolecular Non-Bonded Contacts

Atom 1	Atom 2	Distance (Å)
Rh	Rh'	3.340(2)
Rh	H222	2.98
O2	O2'	2.65(1)
H132	H222'	2.40
H216	O2'	2.62
H122	O1	2.25
H222	O1	2.33
H132	O2	2.88
H216	Cℓ1	2.56
H215	Cℓ3	2.91
O1	O1'	3.49(1)
O1	O2'	2.75(1)

Table 14

Selected Intermolecular Contacts

Atom 1	Atom 2	Symmetry Operation (on atom 2)	Distance (Å)
H115	H236	$\bar{x}+1, \bar{y}, \bar{z}+1$	2.43
H223	H223	$\bar{x}, \bar{y}, z-1$	2.46
H115	H336	$\bar{x}+1, \bar{y}, \bar{z}+1$	2.43

Fig. 5

A General View of, $[(O_2)RhCl(P(C_6H_5)_3)_2]_2$

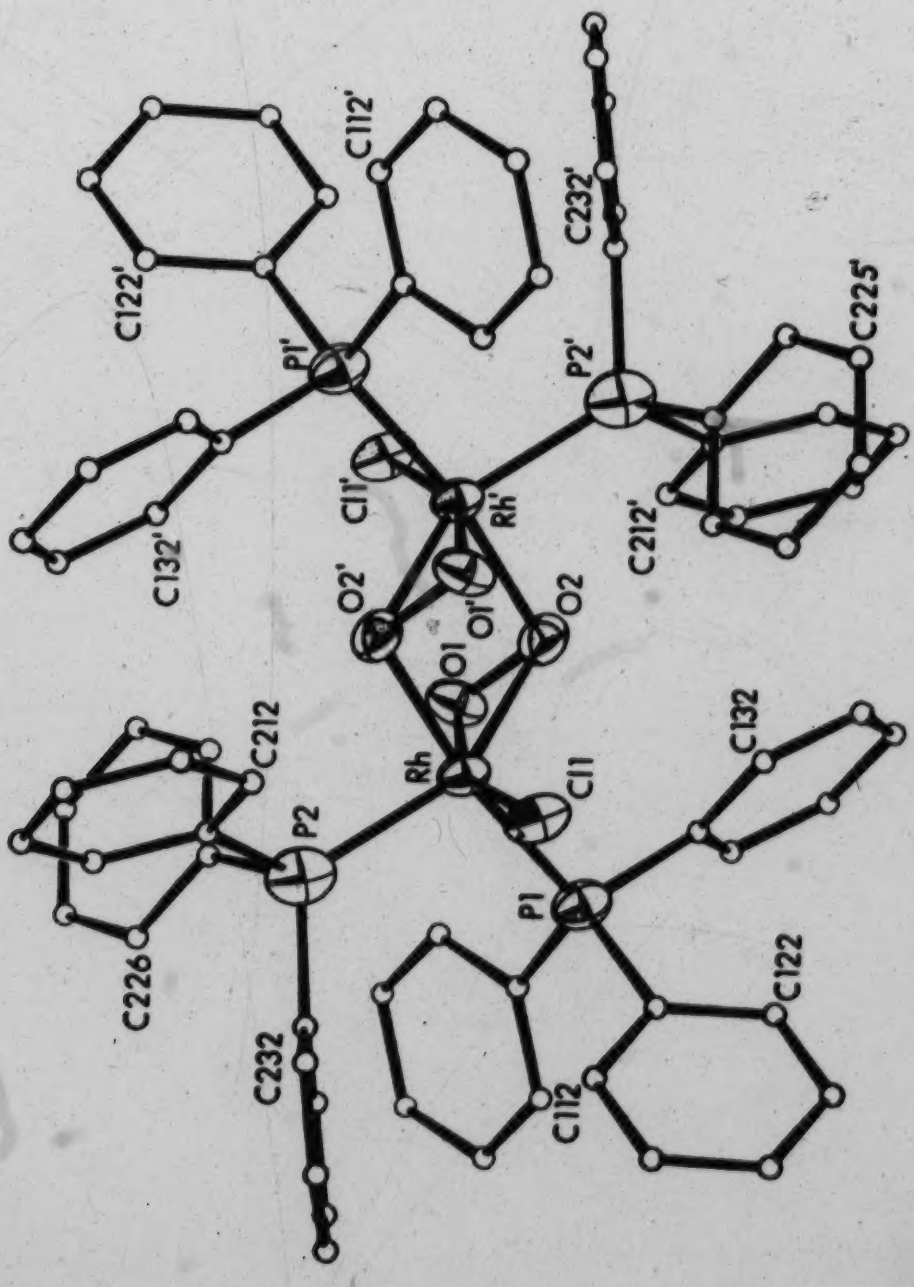


Fig. 6

Dioxygen Bridging Geometry

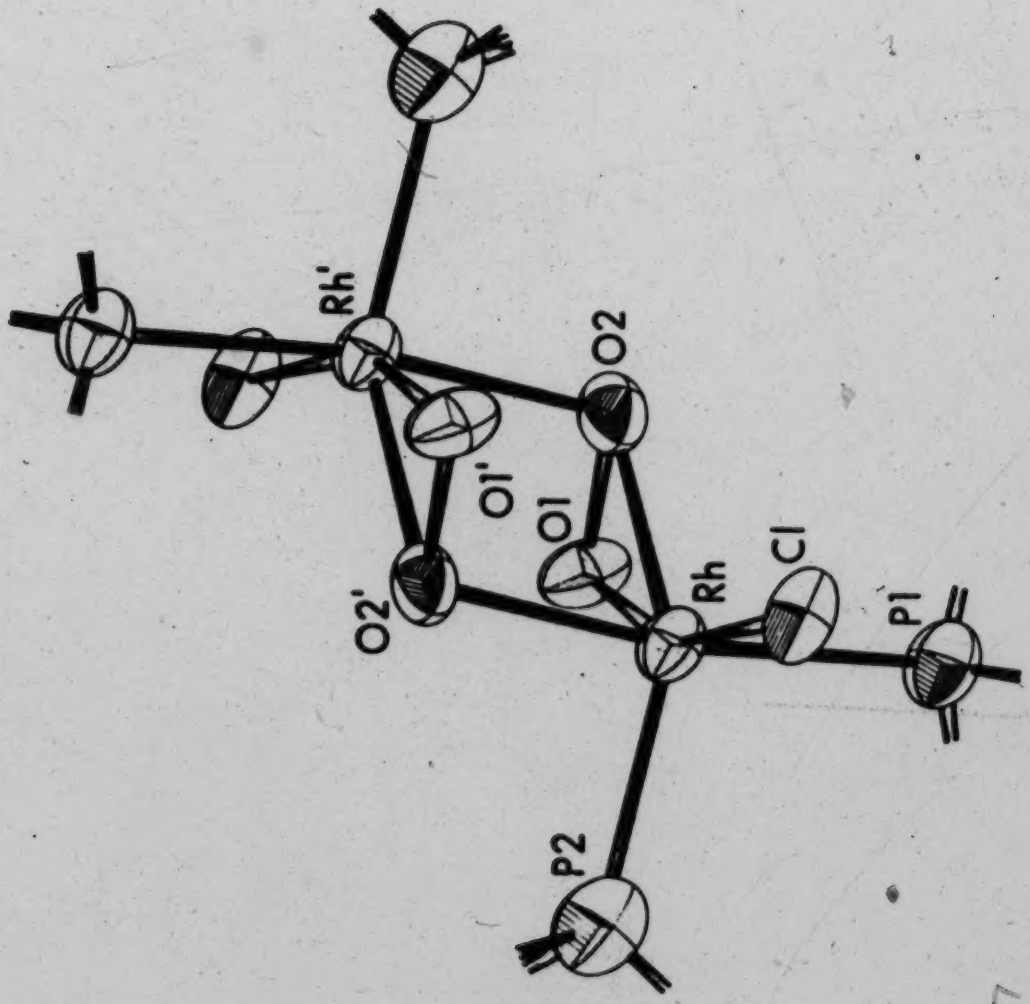
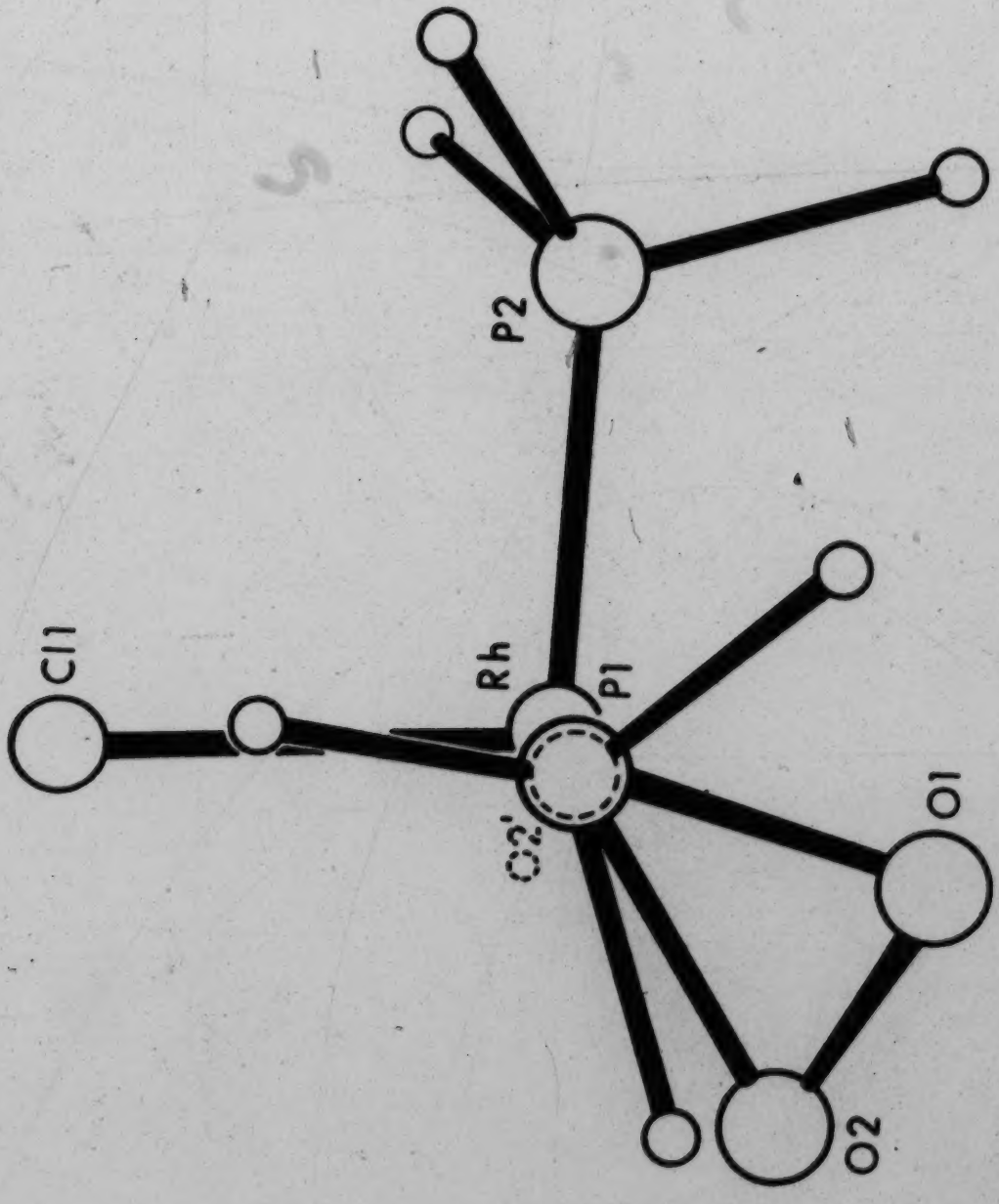


Fig. 7

Subunit Viewed down P1-O2' Direction



Discussion

The structure (Fig. 5) was found to contain dimeric units, situated at inversion centers in the unit cell. The methylene chloride molecule is situated at least 5.6 Å from the central coordination sphere and thus is in no way coordinated to the rhodium atoms. The overall geometry of each subunit can be described as a distorted trigonal bipyramid assuming that the coordinated dioxygen molecule is considered to occupy a single coordination site. The rhodium atoms obey the effective atomic number rule and are coordinatively saturated.

Five coordinate dioxygen species are not particularly unusual (Table 3), however the manner in which this compound achieves this geometry is most unexpected and quite novel. The three equatorial positions of the trigonal bipyramidal subunit are occupied by a triphenylphosphine, a chlorine atom and the coordinated dioxygen molecule in keeping with the similar iridium dioxygen complexes [17-19] (also containing equatorially coordinated dioxygen). The axial coordination sites are occupied by another triphenylphosphine and an oxygen atom from the dioxygen molecule coordinated to the rhodium related by the inversion center. Thus the coordinated dioxygen molecules act as bridging ligands between the rhodium atoms (Fig. 6), with one oxygen atom of each molecule being coordinated in the usual manner for a π-bonded di-

atomic ligand, whereas the other atom although posessing a similar geometric arrangement is also able, *via* a third bond to bridge the two rhodium atoms.

The previously known π-bonded dioxygen derivatives of Vaska's compound and its analogues [33] contain similar geometry but not the bridging bond, whilst O_2F_2 [81] and some of the dioxygen bridged cobalt complexes [97-100] contain fairly similar peroxo symmetry to the bridge without the π-geometry.

In the purely π-bonded dioxygen species dioxygen molecules are situated so that the metal-oxygen distances are equivalent (although some of these complexes [18,19] are disordered and thus any differences in these distances would have been impossible to detect). This is not the case in this complex as the two rhodium-oxygen bond lengths within the same subunit, (Rh-O1, 1.973(7); Rh-O2, 2.195(7) Å) are significantly different. The shorter bond is between the rhodium atom and the oxygen not participating in bridging. The rhodium-oxygen distances to the symmetry related subunit are: (Rh'-O1, 2.778(7); Rh'-O2, 2.069(7) Å). These values indicate that the dioxygen molecules are not perpendicular to the rhodium-rhodium vector as for example had been postulated originally by Vannerberg and Brosset [79] for the structure of $[(NH_3)_5CoO_2Co(NH_3)_5](NO_3)_5$. The rhodium-rhodium distance is 3.340(2) Å and thus is too

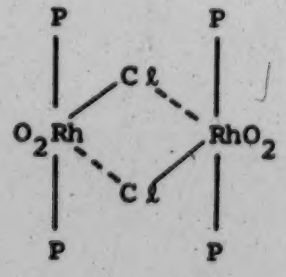
long for a metal-metal bond [117,118]. Discussion of the rhodium-phosphorus and rhodium-chlorine bond lengths, which appear normal, is deferred until Chapter VI.

Using the conventional molecular orbital scheme for dioxygen in the coordinated state [46], the dioxygen molecule may be considered as having the initial configuration $\pi^{*2}\pi^{*0}$ instead of the usual paramagnetic ground state with two unpaired electrons ($\pi^{*1}\pi^{*1}$). The bonding within the fragment RhO1O2 could then be described (according to Griffith [64]) as involving a donation from the ligand to the metal from a fully occupied π-orbital accompanied by back donation from the metal to the empty dioxygen π^* orbital. This model has been widely used to explain a large variation in dioxygen bond lengths. The greater the amount of back donation, the longer the expected oxygen-oxygen bond length would be, assuming either: (1) a fairly constant ligand-metal donation, or (2) the normal synergic interaction [18]. Thus the iridium complexes [17,19] with variations in the oxygen-oxygen bond lengths of from 1.30(3) Å to 1.66(3) Å could be viewed as containing a superoxide ion (O_2^-) in the first case and a peroxide ion (O_2^{2-}) in the second. These increases in bond length would be expected from a simple bond-order calculation.

The retention of Griffith's model seems desir-

able for this complex and the bridging nature of the dioxygen ligand may be explained by observing that the filled π^* orbital (of the dioxygen ligand) not taking part in overlap with the first rhodium atom would be perpendicular to the RhOlO2 plane and thus in a position favourable for the formation of a σ-bond to the neighbouring rhodium. The observed angles of 103.4(5)° for O1O2Rh′ and 103.0(3)° (RhO2Rh′) seem reasonable when the electron density plots for the molecular orbitals of dioxygen [49] are considered. This particular model could accommodate a wide range of O1O2Rh′ angles as it is possible for the filled π-orbitals of the dioxygen to also donate electrons to the second rhodium atom and the observed angle could be considered as a compromise between the two possible bonding extremes.

It is interesting that a *bis*-chloro bridged species (structure 1) does not form even though it might appear equally feasible.



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The preference for the dioxygen bridge suggests that there is a particularly suitable energy relationship between the occupied π^* orbital of the dioxygen molecule and the dz^2 orbital of the rhodium atom (the "z" axis being defined as the pseudothreefold rotation axis of the trigonal bipyramidal subunit). This is supported by the chemical behaviour of the complex as it is inert to either strong acid or base.

The bonding description does not allow a detailed discussion of the oxygen-oxygen bond length as π^* donation to the neighbouring rhodium would decrease the oxygen-oxygen bond length whereas π as a donor would have an opposing effect. In addition the back donation from the metal to the empty π^* orbital could vary. Comparisons with the similar complex $[(O_2)RhCl(P(C_6H_5)_3)_3]$ should prove meaningful and these are made in Chapter IV.

An alternate method of describing the structure of $[(O_2)RhCl(P(C_6H_5)_3)_2]_2$ would be to consider the rhodium as Rh(III) and the dioxygen molecule as a chelating peroxide ion, the bridges being formed from one of the lone pairs of one oxygen atom of each peroxide ion. This could then be viewed as partially analogous to the bent dioxygen cobalt species [65] containing only a π^* donor bond as discussed in Chapter I.

The steric requirements of triphenylphosphine have been discussed by Tolman [119]. The wide Tolman angle

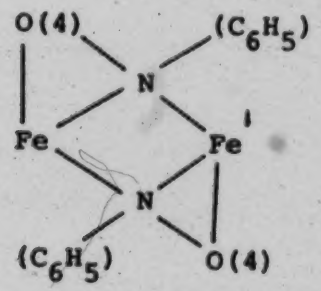
of 145 ± 2 for a single ligand suggests that a *cis* pair of triphenylphosphines (P1-Rh-P2, 100.2(1)°) would have to be interlocked. The hydrogen-hydrogen non-bonded contacts (Tables 13 and 14) are all longer than the sum of their van der Waals radii [120]. A number of other close intramolecular contacts were observed (Cl1-H216, 2.56; O1-H122, 2.25; O1-H222, 2.33; Rh-H222, 2.98 Å) with the closest intramolecular chlorine-hydrogen contact (Cl1-H224(x,y,z+1)) being 2.84 Å. The chlorine-hydrogen contacts are similar to those found in the structure of $RhCl(CS)(P(C_6H_5)_3)_2$ [121]. All contacts are not believed to represent any attraction, but rather to reflect the difficulty of accomodating two bulky ligands in a mutually *cis* arrangement.

The geometry of the methylene chloride molecule is in acceptable agreement with literature values [122,123] despite the deficiencies in the model. The molecule does not appear to be coordinated in any way to the rhodium complex.

The dimeric species reported here cannot represent the major species present in solution as indicated by its insolubility. When oxygen is passed through solutions of $RhCl(P(C_6H_5)_3)_3$ the formation of the dioxygen dimer from the $(O_2)RhCl(P(C_6H_5)_3)_2$ monomer would be expected to be a slow reaction in view of the highly specific geometry required.

A nitroso complex $[Fe(CO)_3(NO)(C_6H_5)]_2$ [125] (2)

published at the same time as the dioxygen dimer [126] has certain similarities in structure.



2

The nitroso group is located with the nitrogen atom bonded in an analogous manner to the dioxygen dimer O2 atom. The geometry of the nitrosyl group is interesting as the iron-oxygen distances of 1.91(1) Å and 2.73(1) Å plus the two angles (Fe-N-Fe', 103.1(3)° and Fe-N-O(4), 104.6(5)°) closely resemble the equivalent values in the dioxygen complex. The geometries are thus extremely similar except for the expected differences in interatomic bond lengths and the equality of the two iron-nitrogen distances (Fe-N, 2.02(1); Fe'-N, 1.98(1) Å). No detailed bonding explanations were given. Other possibly similar dioxygen species are $Rh(P(C_6H_5)_3)_3O_2$ [127] which is diamagnetic, explosive and probably dimeric and $[(O_2)M(tert\text{-}BuNC)_2]_n$ [78], M = Ni, Pd. The latter polymeric species was postulated from highly unreliable data.

Further comparisons of the *bis*-phosphine

dioxygen dimer with other similar complexes are included in Chapter IV and similarities to the parent complex $RhCl(P(C_6H_5)_3)_3$ are examined in Chapter VI.

CHAPTER IV

The Crystal and Molecular Structures of $[(O_2)RhCl(P(C_6H_5)_3)_3 \cdot 2CH_2Cl_2]$

Experimental

Crystals of $(O_2)RhCl(P(C_6H_5)_3)_3$ were prepared according to the method described in Chapter II. They were examined under a microscope and found to be yellow needles, usually arranged in clusters. After considerable searching a single crystal was found and cut to the desired length of approximately 0.2 mm. This crystal was then mounted on the end of a thin glass fibre so that the needle axis was coincident with the rotation axis of the goniometer head.

Examination of preliminary Weissenberg and precession photographs indicated that the crystal possessed orthorhombic symmetry. The systematic absences ($hk0$, $h = 2n + 1$; $h0l$, $l = 2n + 1$; $0kl$, $k = 2n + 1$) were consistent with the unique choice of the space group *vis* Pbca. The crystal was mounted on a Picker manual diffractometer so that the "b" axis (needle axis) was coincident with the diffractometer ϕ axis. Precise lattice parameters and their estimated standard deviations were determined as a, 24.817(4); b, 18.359(2); c, 23.200(4) Å from the setting angles of twelve accurately centered high angle reflections at 22°C. All peaks showed good

resolution of the $K\alpha_1$, $K\alpha_2$ doublet and only the α_1 peaks (λ, 1.54051 Å) were used. The density of the complex was determined by the flotation method in aqueous potassium iodide as ρ_{obs}, 1.411 g-cm^{-3} which is in excellent agreement with the calculated density of 1.416 g-cm^{-3} assuming eight formula units per unit cell. There are consequently no restrictions on the position or orientation of the formula unit in this space group since the number of general positions is eight.

A careful examination of peak profiles showed no obvious physical defects in the study crystal. Intensity data were collected with copper Kα X-radiation using the coupled $\omega/2\theta$ method with a 2° takeoff angle. The diffractometer was equipped with a graphite crystal monochromator (002 reflecting plane). Each data point was scanned from $(2\theta - 1)°$ to $(2\theta + 1)°$ with a scan speed of 2° per minute. Background counts were estimated from a linear interpolation of 30 second stationary counts taken at the limits of the scan. During the data collection, the intensities of six reflections were monitored at periodic intervals to allow for correction of crystal decomposition and to detect crystal misalignment. Data were only measured to 80° in 2θ as indicated by the preliminary photography. Data collection was terminated after 1755 reflections for this first crystal when the standard reflections had decreased in intensity by 10 - 20%.

The crystal faces were identified as the forms {100}, {010} and {001}, and the perpendicular distances between the opposite members of each form were measured as 0.010, 0.028 and 0.018 cm respectively. The variation in intensity of the 0k0 reflections with the setting angle ϕ was measured to provide experimental evidence for the correctness of subsequent absorption corrections. A second crystal of the same habit and with dimensions (0.008 x 0.009 x 0.032 cm), was used to collect the remaining 1970 reflections. The variation of I_{0k0} with ϕ was studied for this second crystal. All intense reflections with count rates in excess of 10^4 counts per second were remeasured under conditions such that the scattered X-rays did not exceed the linear response range of the scintillation counter.

Finally, representative reflections from the first crystal were remeasured with the second crystal to improve the merging of the two data sets. Both crystals appeared to have similar rates of decomposition (directly proportional to $\sin\theta/\lambda$ and logarithmically related to time) and only decomposed when exposed to X-rays. Of the total 3745 reflections measured, 2073 were found to be statistically reliable using the criterion $I \leq 3$. Decomposition and absorption corrections were then applied (μ = 62.1 cm^{-1}) with the transmission factors varying from 0.517 to 0.637 in the first crystal and from

0.356 to 0.544 in the second. The data were then corrected for Lorentz and polarization effects and the derived structure amplitudes and their standard deviations calculated (p = 0.03) after the two data sets had been scaled.

Solution of Structure and Refinement

A Patterson map was calculated and the atomic coordinates of the rhodium atom found from the Harker line peaks [128] (Table 15). As the "y" and "z" coordinates were approximately 0.25, a large number of peaks were superimposed. Although some evidence of the chlorine was found, only the rhodium atom was included in the first cycle of refinement (R_1, 0.547). The positions of the chlorine atom Cl1 and the three phosphorus atoms were located from an electron density map calculated at this point. The rest of the molecule was found as outlined in Table 16.

The carbon rings were constrained to D_{6h} symmetry, with carbon-carbon bond lengths of 1.392 Å, to minimize the number of parameters. The temperature factors of all atoms were not refined until R_1 = 0.178 (Table 17) as unrealistic values were obtained before all atoms were included. The values used (Rh, Cl, P; 2.5; C, 5.0) were similar to the final equivalent isotropic temperature factors obtained for the dimeric species

(Chapter III). The atomic scattering factors for rhodium, chlorine, phosphorus and carbon atoms were those of the neutral atoms and included the real and imaginary terms for anomalous dispersion for the rhodium, chlorine and phosphorus atoms. These scattering factors were obtained from Cromer's coefficients [111]. Hydrogen atoms were included at their calculated positions with carbon-hydrogen bond lengths of 1.0 Å and isotropic thermal parameters set 10% larger than those of the carbon atoms to which they were attached. The hydrogen scattering factors were those of Mason and Robertson [113].

Refinement was considered complete when the maximum parameter shift was one seventh of the corresponding standard deviation. The standard deviation of an observation of unit weight was 1.79 at convergence, which is reasonable in view of the constraints imposed upon the model. A final electron density difference map was calculated and the largest positive and negative peaks (0.38 and -0.36 $e.Å^{-3}$; cf carbon ~$3e.Å^{-3}$) were located near the methylene chloride molecules.

Table 15

Assignment of Patterson Map Peaks

Peak Coordinates u	v	w	Rel. Height (origin=999)	Assignment	Calc. Height	Calc. Coordinates (from Solution)		
0.168,	0.500,	0.500	174	1/2-2x,1/2,1/2	159	0.168,	0.500,	0.500
-0.168,	0.500,	0.500	180	1/2+2x,1/2,1/2	159	-0.168,	0.500,	0.500
0.00,	0.00,	0.00		0,1/2+2y,0	159	0.0,	-0.030,	0.0
..	..	..		0,1/2-2y,0	159	0.0,	0.030,	0.0
0.504,	0.00,	0.00	384	1/2,0,1/2+2z	159	0.500,	0.00,	-0.026
..	..	..	(total)	1/2,0,1/2-2z	159	0.500,	0.00,	0.026
..	..	..		1/2,1/2+2y,1/2+2z	79	0.500,	-0.030,	-0.030
..	..	..		1/2,1/2-2y,1/2+2z	79	0.500,	0.030,	-0.030
..	..	..		1/2,1/2+2y,1/2-2z	79	0.500,	-0.030,	0.030
..	..	..		1/2,1/2-2y,1/2-2z	79	0.500,	0.030,	0.030
0.324,	0.500,	0.500	128	2x,1/2,2z	79	0.332,	0.500,	0.474
..	..	..		2x,1/2,$2\bar{z}$	79	0.332,	0.500,	0.526

(Table continued)

Table 15 continued

Peak Coordinates			Rel. Height (origin=999)	Assignment	Calc. Height	Calc. Coordinates (from Solution)		
u	v	w						
..	..	..		2x,2y,2z	40	0.332,	0.470,	0.474
..	..	..		2x,2y,$2\bar{z}$	40	0.332,	0.470,	0.526
..	..	..		2x,$2\bar{y}$,2z	40	0.332,	0.520,	0.474
..	..	..		2x,$2\bar{y}$,2z	40	0.332,	0.530,	0.526

rhodium solution x = 0.166, y = 0.235, z = 0.237

Table 16

Structure Solution Sequence

Refinement Cycle	Atoms used in Refinement	R_1	Atoms found in Diff. Map
1	Rh	0.547	Cℓ1,P1,P2,P3
2	Rh,Cℓ1,P1,P2,P3	0.439	O1,O2,Cℓ2,Cℓ3,Cℓ4,Cℓ5,C111-C116, C121-C126,C311-C316
3	Rh,Cℓ1,P1,P2,P3,O1,O2,Cℓ2, Cℓ3,Cℓ4,Cℓ5,C111-C116, C121-C126,C311-C316	0.406	
4	..	0.305	C131-C136,C211-C216,C221-C226
5	Rh,Cℓ1,P1,P2,P3,O1,O2,Cℓ2, Cℓ3,Cℓ4,Cℓ5,C111-C116,C121-C126,C131-C136,C211-C216, C221-C226,C311-C316	0.243	C231-C236,C321-C326,C331-C336, C1,C2
6	Rh,Cℓ1,P1,P2,P3,O1,O2,Cℓ2, Cℓ3,Cℓ4,Cℓ5,C1,C2,C111-C116, C121-C126,C131-C136,C211-C216 C231-C236,C311-C316,C321-C326, C331-C336	0.178	

Table 17

Structure Refinement Sequence

Refinement Cycle	Model	R_1	R_2
6	All atoms included, isotropic temperature factors held constant	0.178	0.242
7	Temperature factors refined	0.111	0.134
8	Anomalous dispersion correction	0.092	0.109
9	Central atoms given anisotropic thermal parameters	0.073	0.087
10	Hydrogen atoms included	0.060	0.072
11	.. .. ..	0.053	0.064
12	.. .. ..	0.049	0.059

Results

Table 18 gives the observed ($|F_o|$) and calculated ($|F_c|$) structure amplitudes (electrons x 10). The final atomic coordinates of all atoms are included in Table 19 with the anisotropic thermal parameters (U_{ij}) of the central atoms listed in Table 20. Other tables give the interatomic distances (Table 21), interatomic angles (Table 22) and inter- and intramolecular non-bonded contacts (Tables 23 and 24 respectively) with the standard deviations (as calculated by ORFFE II) of the least significant digit included in parentheses. Bond lengths from the rhodium atom to the ligand atoms were also calculated to include a correction for thermal motion in which the second or lighter atom was assumed to ride on the heavier rhodium.

Fig. 8 shows a general view of the molecule with views down the P1-P3 and Rh-P2 directions (Figs. 9 and 10 respectively) being included.

Table 18

Observed and Calculated Structure Amplitudes

(electrons x 10)

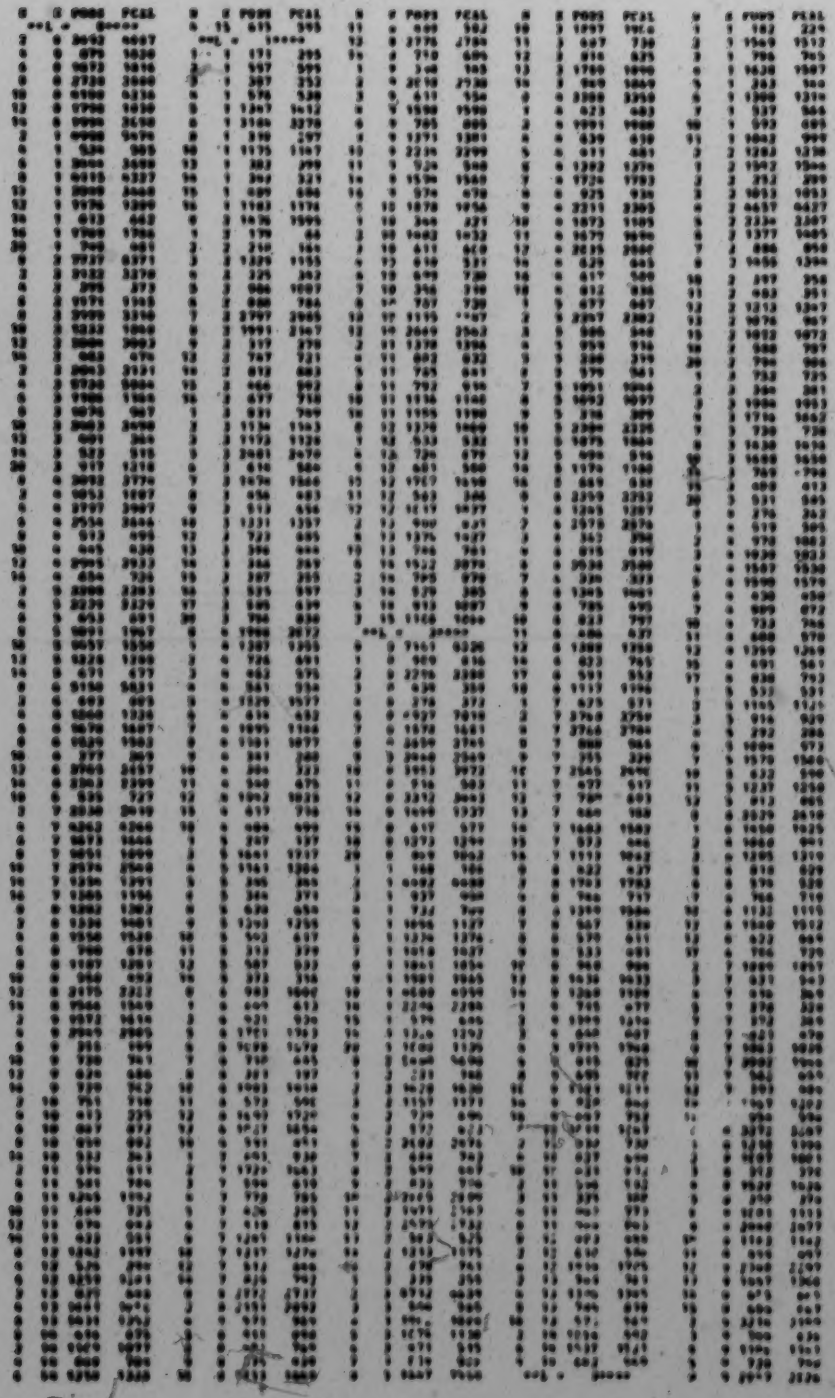


Table 18 continued

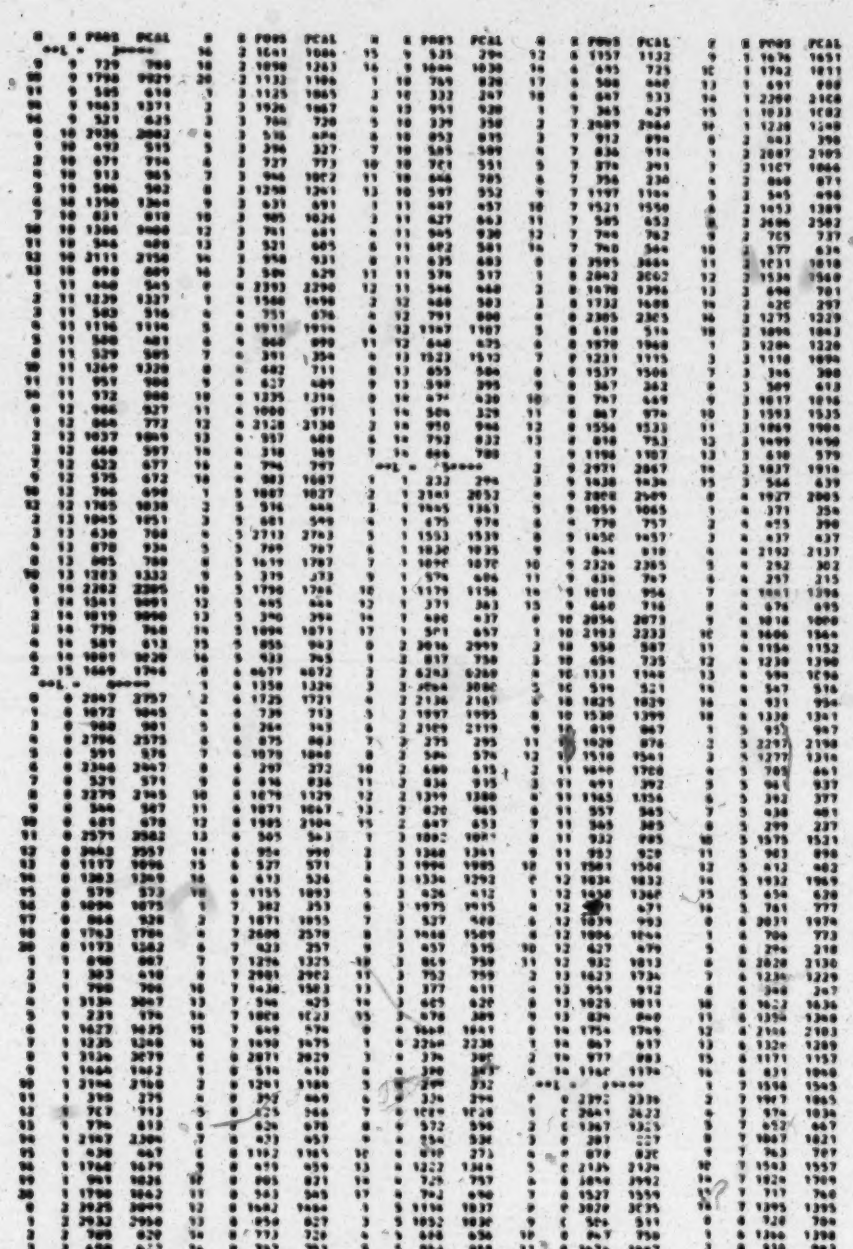


Table 18 continued

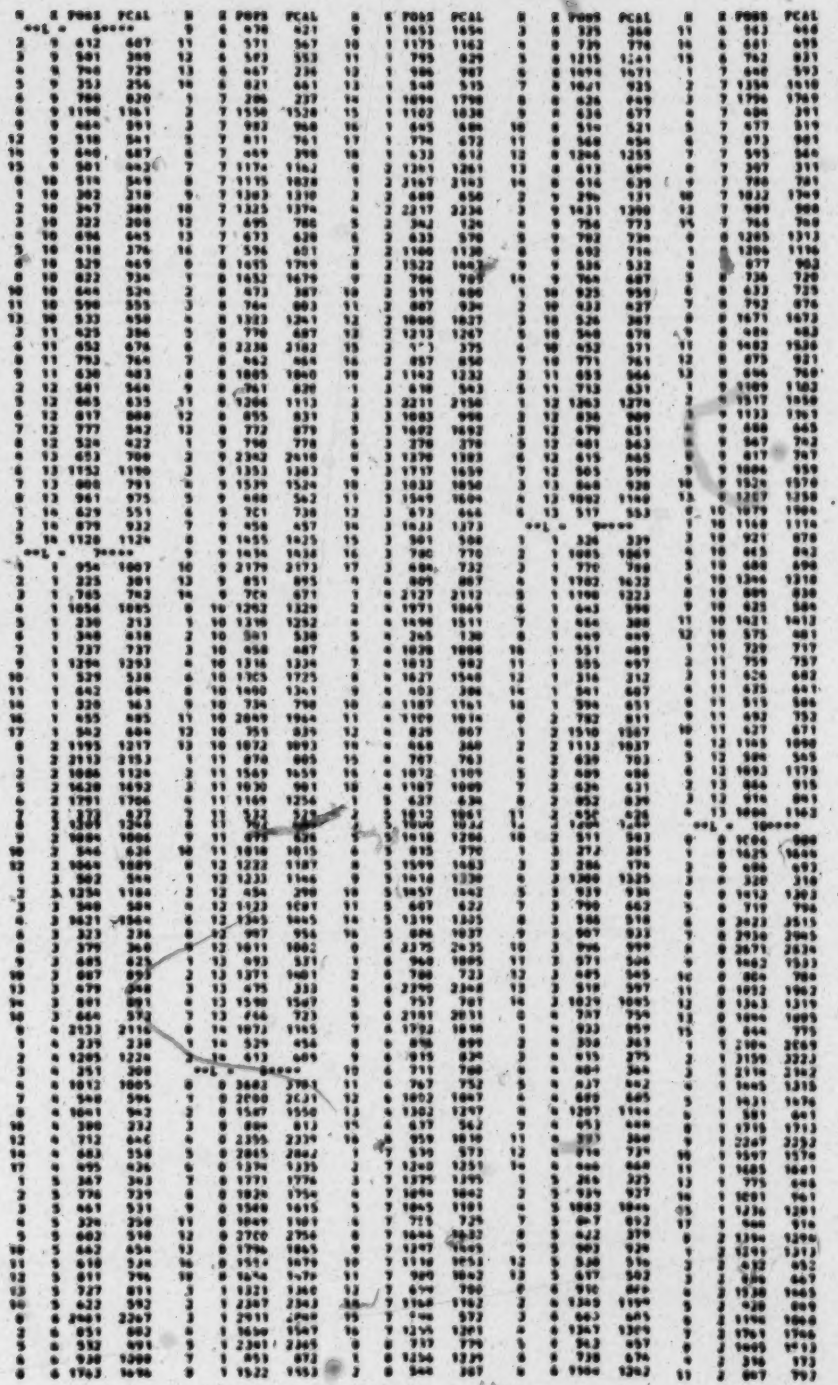


Table 18 continued

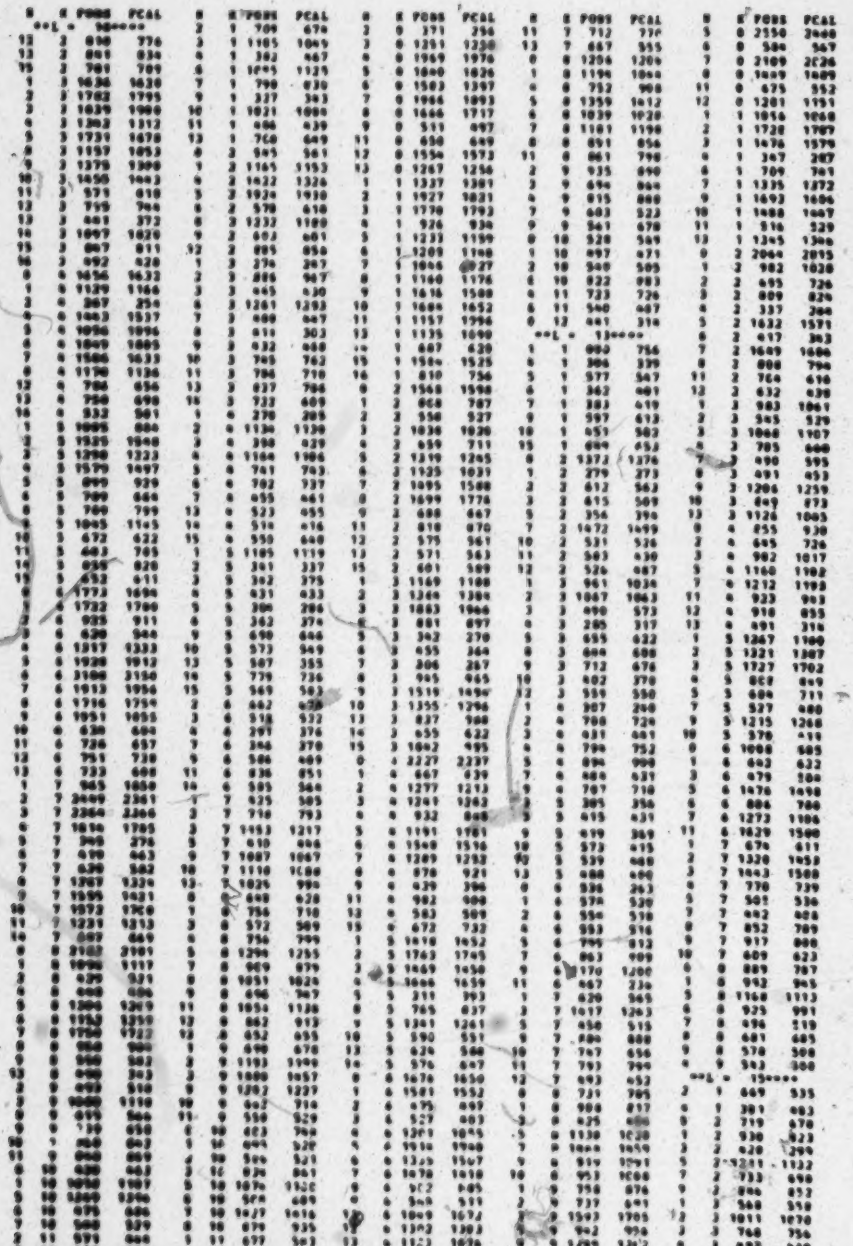


Table 18 continued

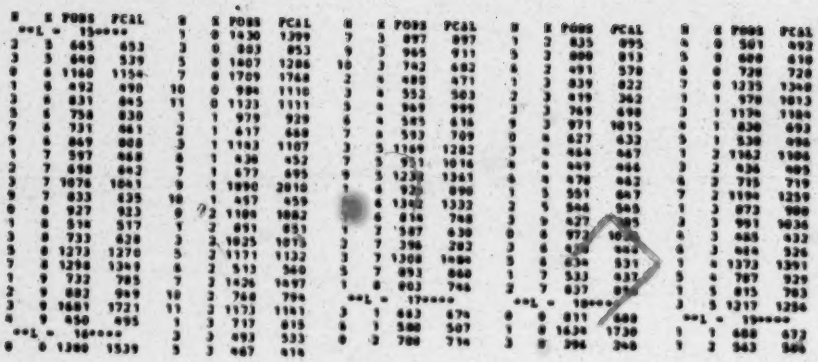


Table 19

Atomic Coordinates and Isotropic Temperature Factors

Name	x	y	z	B
Rh	0.16618(4)	0.23480(5)	0.23730(4)	2.3*
Cℓ1	0.1727(1)	0.1049(2)	0.2386(1)	3.4*
P1	0.0722(1)	0.2154(2)	0.2424(1)	2.8*
P2	0.1877(1)	0.2637(2)	0.3333(1)	2.4*
P3	0.2531(2)	0.2252(2)	0.1938(1)	2.9*
Cℓ2	0.4111(3)	0.2504(5)	0.4869(4)	17.4*
Cℓ3	0.3976(3)	0.0987(4)	0.4933(3)	14.9*
C1	0.3687(9)	0.179(1)	0.506(1)	12.9*
Cℓ4	0.1302(2)	0.4769(3)	0.0778(3)	13.1*
Cℓ5	0.0451(4)	0.3844(4)	0.0444(3)	18.7*
C2	0.0846(9)	0.410(1)	0.1009(9)	11.2*
O1	0.1447(3)	0.2832(4)	0.1595(3)	3.4
O2	0.1534(3)	0.3341(4)	0.2041(3)	2.9

* These values are equivalent isotropic temperature factors corresponding to the anisotropic temperature factors shown in table 20

(Table continued)

Table 19 continued

(a) Phenyl Carbon Rigid Bodies

Name	x	y	z	B
C111	0.0411(7)	0.1660(5)	0.3022(5)	3.4(3)
C112	-0.0131(6)	0.1760(5)	0.3152(3)	6.4(4)
C113	-0.0363(6)	0.1386(6)	0.3612(5)	8.0(5)
C114	-0.0052(7)	0.0912(5)	0.3941(5)	6.1(4)
C115	0.0491(6)	0.0812(5)	0.3811(3)	5.6(4)
C116	0.0723(6)	0.1186(6)	0.3352(5)	4.1(4)
D	5.432(5)	$x^{1\ddagger}$	0.0180(3)	
E	0.372(8)	$y^{1\ddagger}$	0.1286(3)	
F	0.85(1)	$z^{1\ddagger}$	0.3482(3)	
C121	0.0546(4)	0.1579(5)	0.1814(3)	2.4(3)
C122	0.0437(4)	0.0840(5)	0.1880(3)	3.8(4)
C123	0.0327(4)	0.0413(4)	0.1398(5)	4.9(4)
C124	0.0326(4)	0.0725(5)	0.0851(3)	4.9(4)
C125	0.0436(4)	0.1464(5)	0.0786(3)	5.3(4)
C126	0.0546(4)	0.1891(4)	0.1267(5)	4.5(4)
D	0.208(5)	x^{1}	0.0436(2)	
E	1.666(5)	y^{1}	0.1152(3)	
F	2.528(6)	z^{1}	0.1332(3)	
C131	0.0302(4)	0.2949(5)	0.2324(3)	3.4(3)
C132	0.0465(3)	0.3625(6)	0.2533(2)	3.4(3)
C133	0.0142(4)	0.4235(4)	0.2448(4)	4.2(4)

(Table continued)

Table 19 continued

Name	x	y	z	B
C134	-0.0345(4)	0.4169(5)	0.2154(3)	5.5(4)
C135	-0.0508(3)	0.3493(6)	0.1945(2)	7.0(5)
C136	-0.0185(4)	0.2883(4)	0.2030(4)	6.4(4)
D	2.956(5)	x^1	-0.0022(3)	
E	2.644(5)	y^1	0.3559(4)	
F	2.183(7)	z^1	0.2239(2)	
C211	0.1364(3)	0.3164(6)	0.3707(3)	2.4(3)
C212	0.1371(3)	0.3921(6)	0.3727(3)	3.6(4)
C213	0.0948(4)	0.4298(3)	0.3985(4)	4.5(4)
C214	0.0518(3)	0.3916(6)	0.4224(3)	4.5(4)
C215	0.0512(3)	0.3158(6)	0.4204(3)	4.6(4)
C216	0.0934(4)	0.2782(3)	0.3945(4)	3.9(4)
D	0.035(5)	x^1	0.0941(2)	
E	0.499(5)	y^1	0.3540(3)	
F	5.764(7)	z^1	0.3965(2)	
C221	0.2445(3)	0.3293(4)	0.3348(3)	2.5(3)
C222	0.2447(4)	0.3828(5)	0.2922(3)	2.6(3)
C223	0.2830(4)	0.4381(4)	0.2937(4)	3.2(3)
C224	0.3211(3)	0.4400(4)	0.3377(3)	3.4(3)
C225	0.3209(4)	0.3866(5)	0.3803(3)	3.4(3)
C226	0.2825(4)	0.3312(4)	0.3788(4)	2.7(3)
D	0.594(5)	x^1	0.2827(2)	
E	2.300(6)	y^1	0.3846(3)	
F	5.206(7)	z^1	0.3363(2)	

(Table continued)

Table 19 continued

Name	x	y	z	B
C231	0.2074(4)	0.1967(5)	0.3875(4)	2.2(3)
C232	0.2318(4)	0.1319(5)	0.3706(3)	3.3(3)
C233	0.2492(4)	0.0823(4)	0.4121(5)	5.5(4)
C234	0.2421(4)	0.0976(5)	0.4704(4)	5.3(4)
C235	0.2176(4)	0.1625(5)	0.4872(3)	5.7(4)
C236	0.2003(4)	0.2120(4)	0.4457(5)	3.9(4)
D	2.677(6)	x^1	0.2247(2)	
E	1.545(6)	y^1	0.1472(3)	
F	5.464(7)	z^1	0.4289(3)	
C311	0.2469(7)	0.1793(4)	0.1236(5)	2.7(3)
C312	0.1977(5)	0.1526(5)	0.1039(7)	3.3(3)
C313	0.1949(4)	0.1171(5)	0.0509(4)	4.5(4)
C314	0.2412(7)	0.1084(4)	0.0177(5)	3.9(4)
C315	0.2903(5)	0.1352(5)	0.0375(7)	5.4(4)
C316	0.2931(4)	0.1707(5)	0.0905(4)	4.5(4)
D	1.062(5)	x^1	0.2440(3)	
E	0.38(1)	y^1	0.1439(2)	
F	1.86(1)	z^1	0.0707(2)	
C321	0.3020(4)	0.1683(5)	0.2319(3)	2.5(3)
C322	0.3099(4)	0.0958(6)	0.2164(3)	4.2(4)
C323	0.3463(4)	0.0529(4)	0.2470(4)	5.7(4)
C324	0.3747(4)	0.0825(5)	0.2931(3)	5.5(4)
C325	0.3668(4)	0.1550(6)	0.3086(3)	4.8(4)

(Table continued)

Table 19 continued

Name	x	y	z	B
C236	0.3304(4)	0.1979(4)	0.2780(4)	3.9(4)
D	2.861(5)	x^1	0.3383(2)	
E	2.276(5)	y^1	0.1254(3)	
F	5.654(7)	z^1	0.2625(2)	
C331	0.2902(4)	0.3077(4)	0.1720(3)	3.1(3)
C332	0.3452(4)	0.3168(5)	0.1814(3)	4.9(4)
C333	0.3703(4)	0.3814(6)	0.1653(3)	6.1(4)
C334	0.3405(4)	0.4370(4)	0.1399(3)	5.0(4)
C335	0.2855(4)	0.4279(5)	0.1305(3)	4.0(4)
C336	0.2603(3)	0.3632(6)	0.1466(3)	3.0(3)
D	3.536(5)	x^1	0.3153(2)	
E	2.933(5)	y^1	0.3723(3)	
F	1.177(7)	z^1	0.1560(2)	

† Coordinates of center of gravity of ring.

(Table continued)

Table 19 continued

(b) Phenyl Hydrogen Atoms

Name	x	y	z	B
H112	-0.0353	0.2102	0.2915	7.0
H113	-0.0752	0.1460	0.3704	8.8
H114	-0.0219	0.0644	0.4271	6.7
H115	0.0713	0.0471	0.4048	6.2
H116	0.1112	0.1112	0.3259	4.5
D	5.432			
E	0.374			
F	1.890			
H122	0.0437	0.0615	0.2272	4.2
H123	0.0248	-0.0118	0.1444	5.4
H124	0.0247	0.0419	0.0505	5.4
H125	0.0436	0.1689	0.0393	5.8
H126	0.0625	0.2422	0.1221	4.9
D	0.208			
E	0.166			
F	3.576			
H132	0.0815	0.3669	0.2743	3.7
H133	0.0261	0.4719	0.2598	4.6
H134	-0.0576	0.4609	0.2094	6.0
H135	-0.0858	0.3449	0.1734	7.7
H136	-0.0303	0.2399	0.1880	7.0

(Table continued)

Table 19 continued

Name	x	y	z	B
D	2.956			
E	2.644			
F	3.230			
H212	0.1682	0.4194	0.3557	4.0
H213	0.0956	0.4842	0.4000	4.9
H214	0.0215	0.4188	0.4409	4.9
H215	0.0200	0.2886	0.4374	5.0
H216	0.0927	0.2238	0.3931	4.3
D	0.035			
E	0.499			
F	6.811			
H222	0.2172	0.3811	0.2607	2.9
H223	0.2830	0.4763	0.2630	3.5
H224	0.3485	0.4800	0.3385	3.7
H225	0.3483	0.3882	0.4118	3.7
H226	0.2826	0.2930	0.4095	3.0
D	0.594			
E	2.300			
F	6.253			
H232	0.2369	0.1208	0.3288	3.6
H233	0.2667	0.0358	0.4000	6.0
H234	0.2545	0.0622	0.5002	5.8
H235	0.2125	0.1736	0.5290	6.3

(Table continued)

Table 19 continued

Name	x	y	z	B
H236	0.1827	0.2587	0.4577	4.3
D	2.677			
E	1.545			
F	6.511			
H312	0.1644	0.1589	0.1276	3.6
H313	0.1597	0.0979	0.0367	4.9
H314	0.2392	0.0829	-0.0202	4.3
H315	0.3236	0.1289	0.0138	5.9
H316	0.3284	0.1899	0.1048	4.9
D	1.062			
E	0.38			
F	2.90			
H322	0.2894	0.0745	0.1833	4.6
H323	0.3520	0.0009	0.2359	6.3
H324	0.4008	0.0518	0.3150	6.0
H325	0.3872	0.1763	0.3417	5.3
H326	0.3247	0.2499	0.2891	4.3
D	2.861			
E	2.276			
F	6.701			
H332	0.3666	0.2769	0.1998	5.4
H333	0.4098	0.3879	0.1721	6.7
H334	0.3586	0.4834	0.1283	5.5

(Table continued)

Table 19 continued

Name	x	y	z	B
H335	0.2641	0.4678	0.1121	4.4
H336	0.2208	0.3568	0.1398	3.3
D	3.536			
E	2.933			
F	2.224			

Table 20

Anisotropic Temperature Factors ($Å^2 \times 10^3$)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Rh	34.0(9)	24.8(9)	26.8(9)	0.9(7)	- 2.6(7)	3.0(6)
Cl1	51(3)	25(2)	55(2)	4(2)	1(2)	1(2)
P1	41(3)	30(3)	35(3)	2(2)	- 5(2)	2(2)
P2	36(3)	25(3)	30(2)	-2(2)	- 2(2)	5(2)
P3	43(3)	33(3)	33(2)	0(3)	0(2)	4(2)
Cl2	144(6)	186(7)	330(10)	36(6)	6(6)	4(7)
Cl3	182(7)	185(8)	198(7)	37(6)	40(5)	-43(5)
Cl	140(20)	38(15)	312(30)	-7(16)	100(20)	-72(17)
Cl4	142(6)	115(6)	242(7)	20(5)	33(5)	14(5)
Cl5	327(11)	213(8)	172(6)	-54(7)	-119(7)	47(6)
C2	165(21)	123(19)	140(18)	-87(17)	- 66(16)	87(14)

Table 21

Selected Interatomic Distance

Atom 1	Atom	Distance (Å)	
Rh	Cℓ1	2.391(3)	2.401(3)*
Rh	P1	2.362(4)	2.365(4)*
Rh	P2	2.357(3)	2.357(3)*
Rh	P3	2.387(4)	2.391(4)*
Rh	O1	2.081(8)	
Rh	O2	2.005(8)	
P1	C111	1.828(7)	
P1	C121	1.819(7)	
P1	C131	1.809(7)	
P2	C211	1.836(7)	
P2	C221	1.836(7)	
P2	C231	1.818(7)	
P3	C311	1.840(7)	
P3	C321	1.829(7)	
P3	C331	1.842(7)	
O1	O2	1.413(9)	
C1	Cℓ2	1.74(2)	
C1	Cℓ3	1.67(2)	
C2	Cℓ4	1.75(2)	
C2	Cℓ5	1.70(2)	

* A riding correction was performed on these bondlengths with atom 2 assumed to ride on atom 1

Table 22

Selected Intramolecular Angles

Atom 1	Atom 2	Atom 3	Angle (°)
O1	Rh	O2	40.4(3)
O1	Rh	P1	90.0(2)
O1	Rh	P2	101.3(2)
O1	Rh	P3	92.8(2)
O1	Rh	Cℓ1	157.4(2)
O2	Rh	P1	81.7(2)
O2	Rh	P2	141.7(2)
O2	Rh	P3	84.1(2)
O2	Rh	Cℓ1	117.0(2)
P1	Rh	P2	102.7(1)
P1	Rh	P3	154.4(1)
P1	Rh	Cℓ1	85.1(1)
P2	Rh	P3	101.6(1)
P2	Rh	Cℓ1	101.3(1)
P3	Rh	Cℓ1	82.5(1)
Rh	P1	C111	122.0(4)
Rh	P1	C121	106.6(3)
Rh	P1	C131	116.2(4)
Rh	P2	C211	113.4(3)
Rh	P2	C221	110.1(3)
Rh	P2	C231	124.2(3)
Rh	P3	C311	109.4(4)

(Table continued)

Table 22 continued

Atom 1	Atom 2	Atom 3	Angle (°)
Rh	P3	C321	115.9(3)
Rh	P3	C331	120.4(4)
O1	O2	Rh	66.9(4)
O2	O1	Rh	72.7(5)
Rh	O1	C2	157(1)
O2	O1	C2	84(1)
O1	C2	Cℓ4	111(1)
O1	C2	Cℓ5	114(1)
O2	C2	Cℓ4	99(1)
O2	C2	Cℓ5	133(1)
Cℓ2	C1	Cℓ3	111(1)
Cℓ4	C2	Cℓ5	109(1)
P1	C111	C114	179.3(7)
P1	C121	C124	177.0(6)
P1	C131	C134	179.2(6)
P2	C211	C214	176.0(6)
P2	C221	C224	174.1(5)
P2	C231	C234	176.6(6)
P3	C311	C314	178.0(7)
P3	C321	C324	178.2(6)
P3	C331	C334	176.5(7)
C222	H222	O2	157.8
C223	H223	Cℓ1	140.5

(1/2-x, 1/2+y, z)

Table 23

Selected Intramolecular Non-Bonded Contacts

Atom 1	Atom 2	Distance (Å)
Rh	H312	2.90
Cℓ1	H116	2.54
Cℓ1	H232	2.64
Cℓ1	H312	2.77
O11	H126	2.34
C21	H336	2.37
O2	H336	2.28
O2	H222	2.23
O2	H132	2.49
O2	C2	3.26(2)
O1	C2	3.08(2)
H332	H326	2.37

Table 24

Selected Intermolecular Contacts

Atom 1	Atom 4	Symmetry Operation (on atom 2)	Distance (Å)
Cl1	H223	1/2-x, 1/2+y-1, z	2.66
H122	H134	$\bar{x}$, 1/2+y-1, 1/2-z	2.39
H122	H133	$\bar{x}$, 1/2+y-1, 1/2-z	2.41
H136	H325	1/2+x-1, y, 1/2-z	2.45
H213	H324	1/2-x, 1/2+y, z	2.33
H225	H315	x, 1/2-y, 1/2+z	2.46

Fig. 8

A General View of $[(O_2)RhCl(P(C_6H_5)_3)_3 \cdot 2CH_2Cl_2]$

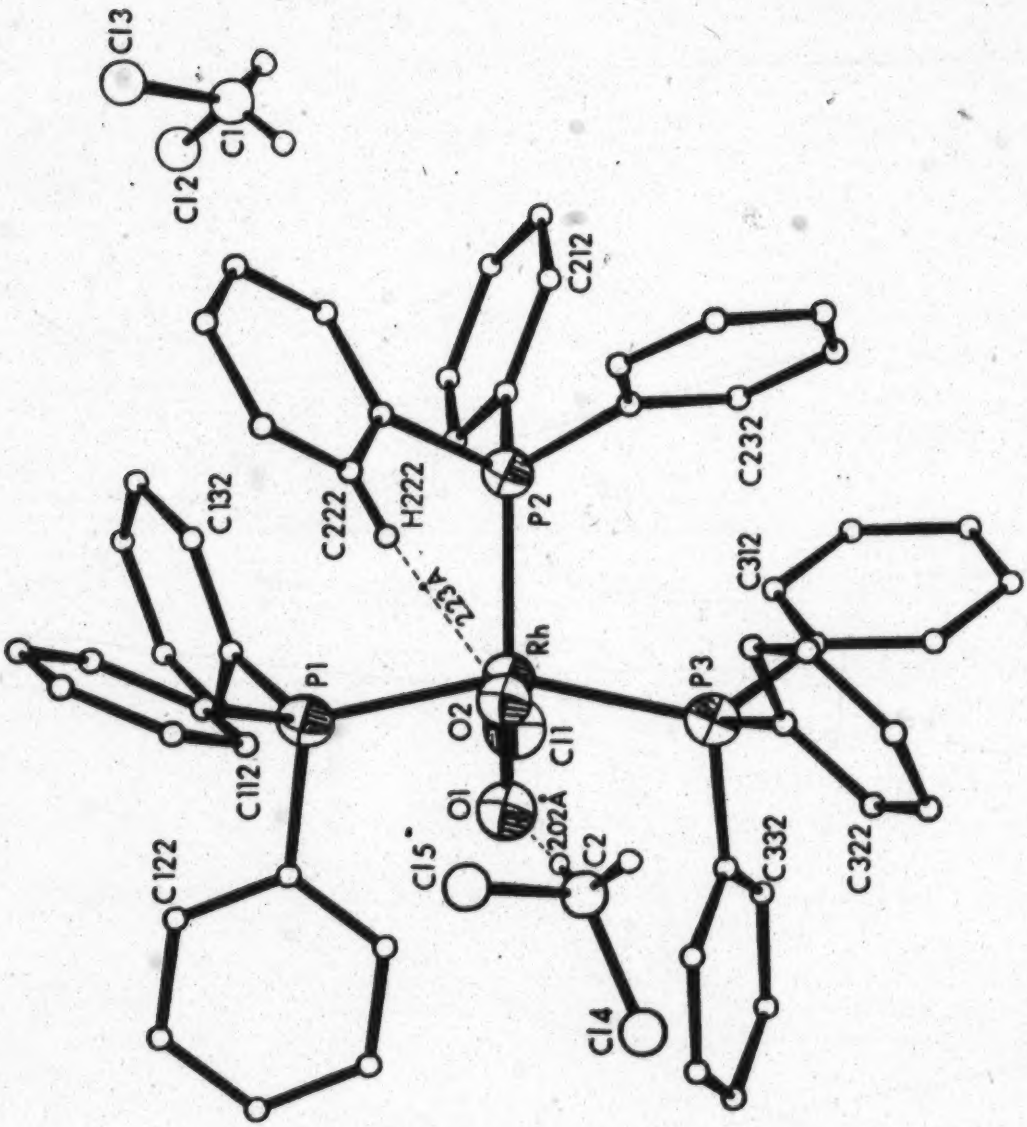


Fig. 9

Equatorial Plane Geometry

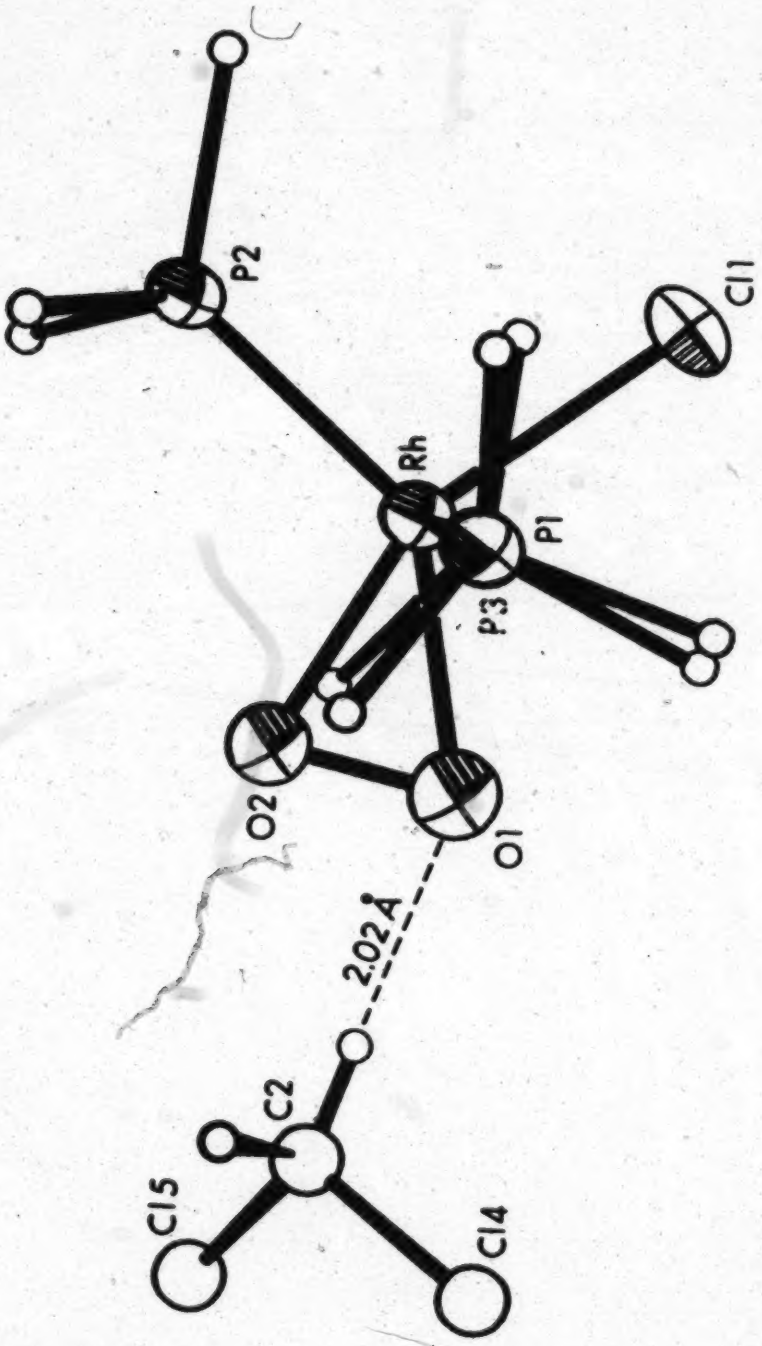
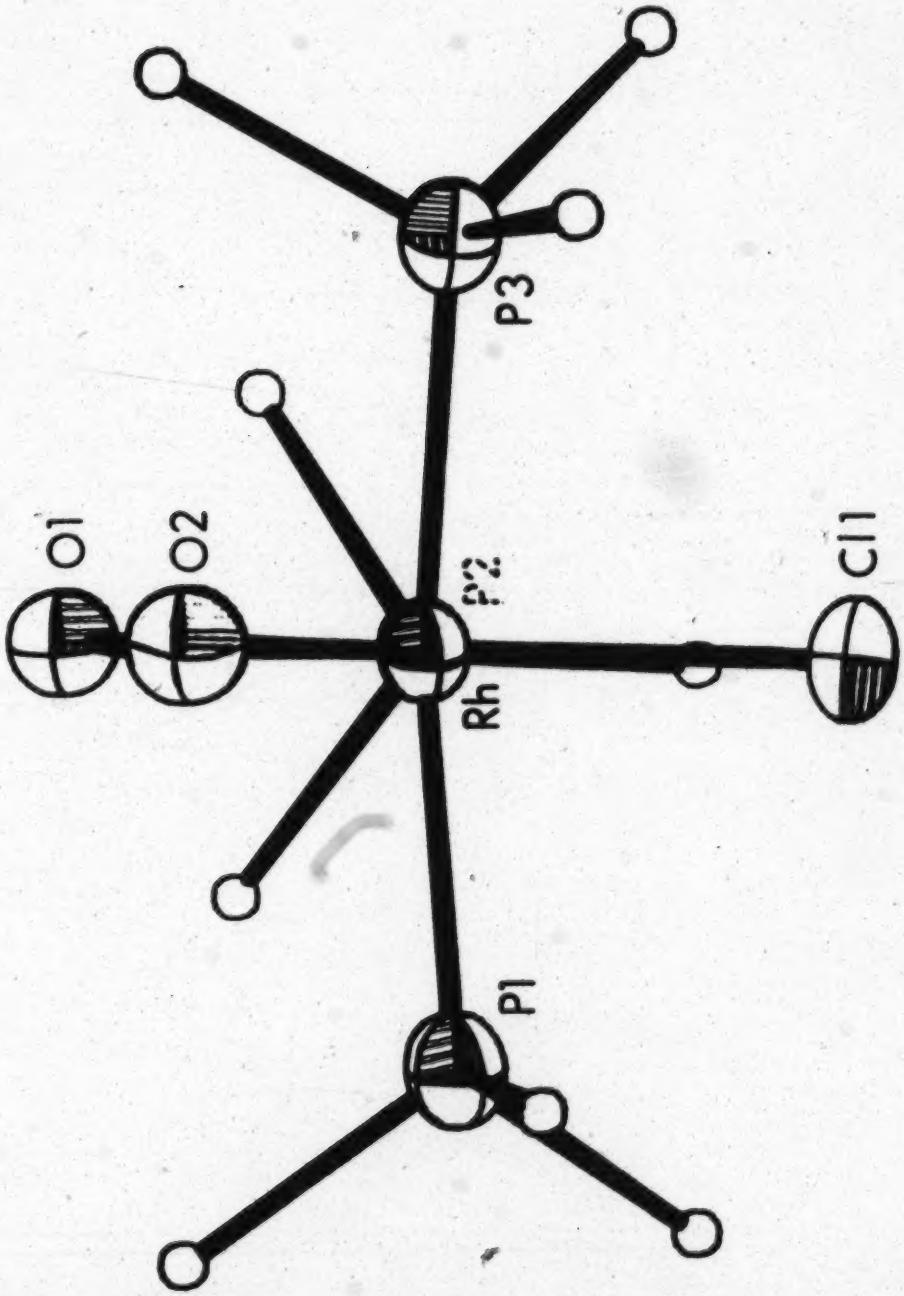


Fig. 10

Central Geometry Viewed down the Rh-P2 Bond



Discussion

The complex has a trigonal bipyramidal structure if dioxygen is treated as occupying a single coordination site (which is the preferred view in this thesis). Alternatively if dioxygen is treated as a bidentate ligand then the structure is approximately octahedral. In the trigonal bipyramidal description, the two axial sites are occupied by triphenylphosphine ligands while the equatorial sites (Fig. 10) contain the third phosphine ligand, the chlorine atom (Cl1) and the dioxygen molecule (with both oxygen atoms in the equatorial plane). The molecule is then coordinatively saturated (Fig. 8).

The rhodium-phosphorus bond lengths (Rh-P1, 2.365(4); Rh-P2, 2.357(3); Rh-P3, 2.391(3) Å) show significant variation. The chemically equivalent axial rhodium-phosphorus (P1 and P3) distances ($\Delta/\sigma \sim 3$) are interesting, however the actual difference is relatively small in absolute terms (0.026 Å) and can probably be ascribed to subtle inter and intramolecular interactions. Similarly statistically significant variations were observed in the structure of $[(Co(2{=}phos)_2(O_2)]^+$ [29] and no chemical significance was assigned. The rhodium-chlorine bond length of 2.401(3) Å is normal for the rhodium complexes discussed in this thesis (see Chapter VI for further discussion). The phosphorus-carbon bond lengths average 1.829 Å which is typical for triphenylphosphine comp-

lexes [17,18,129]. The distribution of these distances was consistent with a standard deviation of 0.010 Å (compared with typical values of ~0.007 Å from the least squares refinement) and hence a small systematic error is indicated. No significant variations were observed when the bond lengths were sorted as to phosphine ligand.

The dioxygen ligand is typical of the π-bonded type (classification (1) in the introduction) and the bonding is rationalized in a manner already discussed in Chapter III. Mason[130] has given a slightly different method of viewing such charge transfer as involving a transition similar to $\pi^4\pi^{*2} \rightarrow \pi^3\pi^{*3}$. Such a description was only meant to illustrate the effects of transfer of charge from the dioxygen bonding to antibonding orbitals by comparison with dioxygen excited states, and not to illustrate the manner of charge transfer. Parshall [131] considered similar species as involving octahedral coordination with two σ-bonds and no π-bonds being present, however such a description does not correlate the oxygen-oxygen bond length with irreversibility of oxygenation whilst the description of Ibers *et al.*,[18] (derived from Griffith's work) [64,132] does.

The oxygen-oxygen bond length is 1.413(9) Å and is not significantly different from that observed for the dimer, 1.438(9) Å. These distances correspond approximately to that expected for a peroxide [89] and the

complex could be viewed as an octahedral rhodium (III) complex, although as mentioned in the introduction such a classification may be unrealistic. The rhodium-oxygen bond lengths (Rh-O1, 2.081(8); Rh-O2, 2.005(8) Å) appear to be significantly different and hence the ligand is not symmetrically attached. This may reflect differences in the *trans*-ligand (O1 is pseudo-*trans* to P2 and O2 is pseudo-*trans* to Cl1). A similar trend is observed in the compound $(O_2)IrCl(CO)(P(C_6H_5)_2(C_2H_5))_2$ [20] where the longer metal oxygen distance is pseudo-*trans* to the better π-bonding ligand (in this case carbon monoxide). Detection of this assymmetry in the structures $(O_2)IrX(CO)(P(C_6H_5)_3)_3$, X = Cl, I [17,19]; is impossible due to the disorder of X and CO that occurs in these crystals.

There are two other features (both short hydrogen-oxygen contacts) that may contribute to the assymmetry of the rhodium-oxygen distances. The first and probably the most important is the contact of 2.02 Å between one methylene chloride hydrogen atom and O1. This is most clearly seen in Fig. 9. This contact is considerably shorter than the sum of the van der Waals radii (2.5 Å) [120] and it is tempting to describe this interaction as a hydrogen bond [133,138]. The orientation of the methylene chloride molecule is such that the calculated position of the hydrogen atom mentioned is approximately on the line joining C2-O1. This is illustrated

by the near equivalence of the angles: Cl4-C2-O1, 111(1)°; Cl5-C2-O1, 114(1)°, which are in good agreement and expected for such an orientation. The second, somewhat longer, contact (O2-H222, 2.23 Å) is intramolecular and hence it is more difficult to decide whether it is attractive or repulsive in nature, however the hydrogen atom is directed towards the oxygen with the ring having the most bending of any phenyl group in the structure (P2-C221-C224, 174.1(5)°) and very low temperature factors. Thus this interaction could possibly be attractive.

The two dioxygen derivatives described in this thesis both demonstrate that coordinated dioxygen is still basic. In the *bis*-phosphine dimer (Chapter III) the coordinated dioxygen forms a donor bond to another rhodium atom, while in the *tris*-phosphine complex the dioxygen molecule is involved in at least one hydrogen bond.

It is probable that neither of these compounds represent the major dioxygen complex formed in solution by the addition of oxygen to $RhCl(P(C_6H_5)_3)_3$. Rather they result from the conditions of crystallisation. The course of events is likely to be that shown below where triphenylphosphine is represented by P.

$$RhP_3Cl + O_2 \rightleftharpoons RhP_3ClO_2 \quad [1]$$

$$RhP_3ClO_2 \rightleftharpoons RhP_2ClO_2 + P \quad [2]$$

$$2RhP_2ClO_2 \rightleftharpoons [RhP_2ClO_2]_2 \quad [3]$$

$$[RhP_2ClO_2]_2 \rightleftharpoons [RhP_2ClO_2]_2\ (s) \quad [4]$$

catalyst

$$P + 1/2\ O_2 \rightleftharpoons PO \quad [5]$$

The equilibrium [2] favours RhP_2ClO_2 and only when the phosphine concentration is high does RhP_3ClO_2 form in sufficient quantity to crystallize. The dimer $[RhP_2ClO_2]_2$ has a very low solubility and hence cannot account for the moderately high concentrations of rhodium in solution. It is probable that reaction [3] is extremely slow in view of the steric factors involved in the formation of the dimer. Hence fresh solutions, formed by the addition of dioxygen to RhP_3Cl, correspond to $RhP_2Cl(O_2)$ in agreement with the earlier osmometric studies [3,37], and this species is thermodynamically more stable than $RhP_3Cl(O_2)$ and kinetically stable with respect to its dimer. Reaction [5] is similar to other reactions [43] producing triphenylphosphine oxide and may explain why free triphenylphosphine is only observed in very low concentrations, whilst the oxide is usually observed in solutions having osmometric molecular weights of ~600 [37].

CHAPTER V

The Crystal and Molecular Structures of the Orange Form of $RhCl(P(C_6H_5)_3)_3$

Experimental

Orange crystals of $RhCl(P(C_6H_5)_3)_3$ were found to have a "lathe" like habit and were arranged in clusters. A suitable crystal was cut from one of these clusters and after examination under a polarizing microscope, it was mounted on the end of a thin glass fibre so that the needle axis was coincident with the goniometer axis.

Examination of preliminary Weissenberg and precession photographs indicated that the compound crystallized in the orthorhombic crystal system (Laué symmetry mmm). Absences were found that satisfied the following set of conditions (hkl, no restrictions; 0kl, k + l = 2n + 1; h0l, h = 2n + 1; hk0, no restrictions). This combination of absences is consistent with the space-groups $Pna2_1$ or Pnam.

The crystal was oriented on a Picker manual diffractometer with the "b" axis coincident with the ϕ axis of the instrument. Several high intensity peaks were scanned for any sign of splitting due to twinning of the crystal (a Laué photograph had been taken earlier as an initial check of the optical examination) and no evidence of twinning was observed.

Lattice parameters were then calculated using diffractometer 2θ values for 13 high angle reflections. The 2θ values were obtained with the independent ω/2θ method and utilized the positive and negative 2θ values. The crude lattice parameters from the photographic study were then subjected to a least squares refinement to give the best fit between the observed and calculated 2θ angles. The high angle reflections were chosen so that there was a large variation in the ϕ and χ angles and in all cases the α_1/α_2 splitting was resolved sufficiently to allow the α_1 peak (λ, 1.54051 Å) to be centered. Lattice parameters were a, 19.470(3); b, 12.689(2); c, 18.202(3) Å; $\alpha = \beta = \gamma$, 90°. The density of the compound was measured by flotation in aqueous potassium iodide solution as 1.363 g-cm^{-3}. The density calculated for four molecules in the unit cell is 1.367 g-cm^{-3}.

Intensity data were collected on a Picker manual diffractometer using copper Kα X-radiation, a 2° takeoff angle and a graphite crystal monochromator (002 reflecting plane). The coupled 2θ/ω method was used with 1 minute scans from (2θ-1)° to (2θ+1)°, 20 second stationary background counts being taken at the limits of the scan. The diffractometer settings were calculated with the programme MIXG2. Data were only collected to 90° in 2θ because of the rapid decrease in the intensities with increasing 2θ, as observed in the

photographic study. During the data collection eight standard reflections were measured at eight hour intervals as an indication of any crystal decomposition (no evidence of which was found) and all reflections having a count rate in excess of 10^4 counts-sec^{-1} were noted. A total of 2212 reflections were measured and of this number 1412 were found to be statistically reliable using the criterion $I \leq 3\sigma$ for rejection. After the data collection the high intensity peaks i.e. those exceeding the linear response range of the detector, were recollected at lower voltages and scaled into the data by comparison with less intense peaks recollected in the same manner. The 0k0 reflections (at $\chi = 90°$) were measured at 10° intervals in ϕ to provide experimental confirmation of the correctness of any absorption correction.

The crystal faces were identified as members of the forms {1,0,0}, {0,1,0}, {0,0,1} and {1,1,0}. The dimensions of the crystal as measured under a microscope were ~0.22 x 0.13 x 0.05 mm. Reflection data were corrected for Lorentz, polarization and absorption effects. Transmission factors varied from 0.805 to 0.550 (μ(CuKα), 47.6 cm^{-1}). Finally the structure amplitudes and their standard deviations were calculated using an uncertainty factor [106] of 0.03.

Structure Solution and Refinement

A three dimensional Patterson map was calculated and carefully examined to resolve the choice of space group. In this case the structural possibilities are: (1) $Pna2_1$ with each molecule occupying a general position and with no constraints on coordinates, (2) Pnam with each molecule occupying a special position and having a mirror plane parallel to the "xy" plane. Special positions involving $\bar{1}$ were not considered a serious option for this molecule.

These two possibilities give rise to the same rhodium-rhodium vectors (1/2 ± 2x, 1/2, 1/2; 1/2, 1/2 ± 2y, 0; ± 2x, ± 2y, 1/2) but in principle they should be resolvable from vectors involving the lighter heavy atoms (phosphorus and chlorine). In this structure three of the heavy ligand atoms have "z" coordinates approximately equal to that of the rhodium and the fourth atom (later shown to be the chlorine atom) has a "z" coordinate definitely different from the "z" coordinate of the rhodium atom albeit by a relatively small amount (Table 25). Thus spacegroup $Pna2_1$ is clearly indicated as the correct spacegroup but the heavy atom fragment ($RhP_3C\ell$) is approximately planar and perpendicular to the "z" axis. The "z" coordinate of the rhodium atom was assigned a value of 0.250 to define the origin of the unit cell in this direction.

This pseudo mirror plane in the fragment of the molecule used for phasing the structure amplitudes produced a pseudo mirror in the electron density map calculated at this stage i.e. the map represented the electron density of the molecule and superimposed upon this was the electron density of the mirror image although not with equal weight. Solution of the structure was slow and required several electron density difference maps to locate all of the atoms. The second image disappeared as the number of atoms in the model increased. The sequence of events in solving the structure is outlined in Table 26.

Subsequent refinements of the model were routine except for incomplete refinement of the phenyl groups due to an error that was specific to rigid bodies in non-centrosymmetric spacegroups in the least squares refinement programme. Once this error had been detected and corrected the structure converged satisfactorily (Table 27). Structure factors for rhodium, chlorine, phosphorus and carbon were calculated using neutral atom scattering factors derived from Cromer's coefficients [111] and included for rhodium, phosphorus and chlorine the real and imaginary terms for anomalous dispersion. The scattering factors of Mason and Robertson [113] were used for the hydrogen atoms. Throughout the calculations the six carbon atoms of each phenyl group were treated as rigid

bodies of D_{6h} symmetry with carbon-carbon bond lengths of 1.392 Å. Hydrogen atoms were included at their calculated positions (carbon-hydrogen bond length, 1.0 Å) with isotropic thermal parameters set at 10% higher than those of the carbon atoms to which they were attached. Due to the shortage of data the number of parameters was a serious concern during the refinement process and the rigid body model for the phenyl groups enabled the number of parameters to be minimized. Anisotropic thermal parameters were introduced for the rhodium, phosphorus and chlorine atoms only.

At convergence (shift/sigma = 0.12) the standard deviation of an observation of unit weight was 1.55 which is certainly acceptable in view of the constraints placed on the model. A final electron density difference map showed no systematic residual peaks with the largest positive and negative peaks being 0.44 and -0.36 e.Å^{-3} respectively (cf. carbon ~3 e.Å^{-3}). These peaks were situated in the vicinity of the 11 and 12 phenyl groups. The correlation matrix was also printed out in this final cycle (R_1 = 0.047; R_2 = 0.053) and high correlations were observed between some carbon temperature factors, however all coordinate correlations were less than 0.2.

Although the space group $Pna2_1$ contains both enantiomers the solutions x, y, z and x, y, $\bar{z}$ (or $\bar{x}$, y, z or x, $\bar{y}$, z) are not equivalent when anomalous scattering

is included in the calculation of the structure factors. Since the space group is polar the 'incorrect' solution would have systematic coordinate errors [135] and hence errors in geometry. For this data set the solution x, y, $\bar{z}$ can be rejected on the basis of a Hamilton R factor ratio test [114] with a confidence level of greater than 99.5%.

The atomic coordinates were then entered into the programme ORFFE II with their respective standard deviations and the interatomic distances and angles (with their corresponding standard deviations) calculated. Rhodium-phosphorus and rhodium-chlorine bond lengths were also calculated including an allowance for thermal motion. In this correction the lighter atom (phosphorus or chlorine) was assumed to ride on the heavier atom (rhodium). This correction was only appreciable for the rhodium-chlorine bond length.

Table 25

Assignment of Patterson Peaks

Peak Coordinates u	v	w	Rel. Height (origin=999)	Assignment	Calc. Height	Calc. Coordinates (from Solution)
0.373,	0.504,	0.494	304	$1/2-2x_a, 1/2, 1/2$	198	0.374, 0.500, 0.500
0.500,	0.440,	0.000	295	$1/2, 1/2-2y_a, 0$	198	0.500, 0.442, 0.000
0.125,	0.060,	0.494	158	$2x_a, 2y_a, 1/2$	99	0.126, 0.058, 0.500
0.012,	0.103,	0.456	73	$x_a+x_b, y_a+y_b, 1/2-z_a+z_b$	37	0.012, 0.102, 0.459
0.385,	0.399,	0.050	68	$1/2-x_a+x_b, 1/2-y_a-y_b, z_a-z_b$	37	0.386, 0.398, 0.041
0.116,	0.046,	0.050	66	$x_a-x_b, -y_a+y_b, z_a-z_b$	37	0.114, 0.044, 0.041
0.382,	0.460,	0.456	60	$1/2-x_a+x_b, 1/2+y_a-y_b, 1/2-z_a+z_b$	37	0.386, 0.456, 0.459
0.397,	0.540,	0.494	56	$1/2+2x_b, 1/2, 1/2$	28	0.398, 0.500, 0.500
0.500,	0.354,	0.000	53	$1/2, 1/2-2y_b, 0$	28	0.500, 0.354, 0.000

Assignment Results a = Rh (0.063, 0.029, 0.250)

b = Cl (-0.051, 0.073, 0.209)

Table 26

Refinement Cycle	Atoms used in Phasing	R_1	New Atoms Located in Corresponding Difference Map
1	Rh, Cℓ	0.425	P1,P2,P3
2	Rh,Cℓ,P1,P2,P3	0.349	C_{111}-C_{116}, C_{131}-C_{136}, C_{211}-C_{216}
3	..	0.304	C_{321}-C_{326}, C_{331}-C_{336}
4	Rh,Cℓ,P1,P2,P3		
5	C_{111}-C_{116}, C_{131}-C_{136}, C_{211}-C_{216}, C_{321}-C_{326}, C_{331}-C_{336}	0.254 0.202	C_{121}-C_{126}, C_{221}-C_{226}, C_{231}-C_{236}, C_{311}-C_{316}
6	all atoms except	0.139	
7	hydrogen included		

Table 27

Refinement Sequence for $RhCl(P(C_6H_5)_3)_3$

Refinement Cycle	Model	R_1	R_2
7	all atoms isotropic	0.092	0.106
8	anomalous dispersion correction applied	0.090	0.104
9	central atoms anisotropic	0.076	0.088
10	.. .. ..	0.069	0.082
11	hydrogen atoms included	0.065	0.076
12	model x, y, $\bar{z}$ tested	0.081	0.097
13	programme error located	0.051	0.057
14[a]	.. .. ..	0.047	0.053
15	model x, y, $\bar{z}$ retested	0.052	0.064

[a] Test of convergence in cycle 14

Maximum coordinate shift as measured in terms of the corresponding standard deviation 0.05

Maximum thermal parameter shift as measured in terms of the corresponding standard deviation 0.12

Results

Table 28 gives the observed ($|F_o|$) and calculated ($|F_c|$) structure amplitudes. The atomic coordinates of all atoms are included in Table 29 with the anisotropic thermal parameters (U_{ij}) of the central atoms being listed in Table 30. Other tables include interatomic distances (Table 31) and interatomic angles (Table 32) with the inter- and intramolecular non-bonded contacts listed in Tables 33 and 34 respectively.

Fig. 11 shows the central coordination geometry viewed perpendicular to the P1-P2-P3 plane. Fig. 12 shows a similar segment of the molecule viewed down the P1-P3 direction whilst Fig. 13 represents a general view of the molecule.

Table 28

Observed and Calculated Structure Amplitudes (electrons x 10)

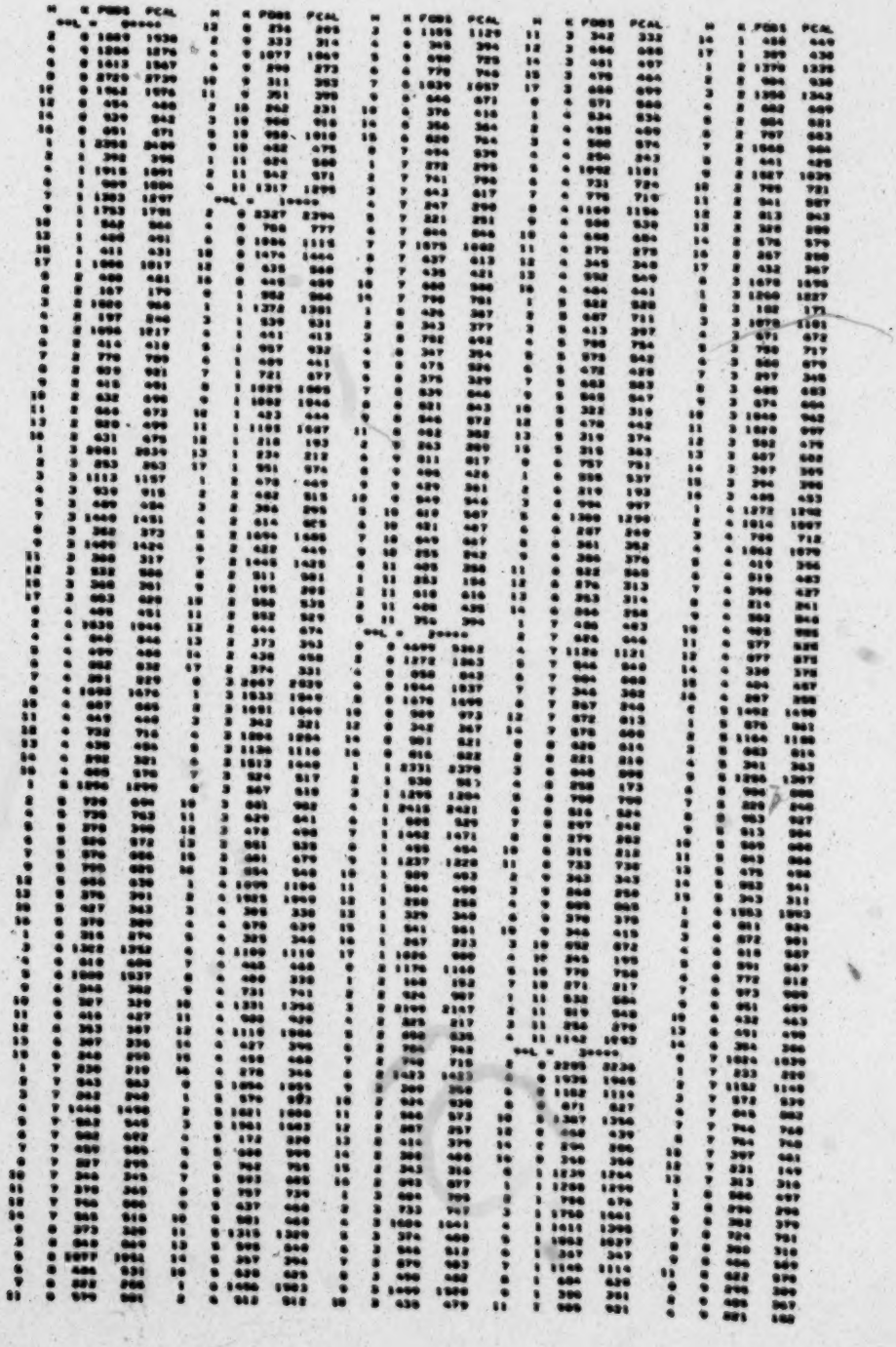


Table 28 continued

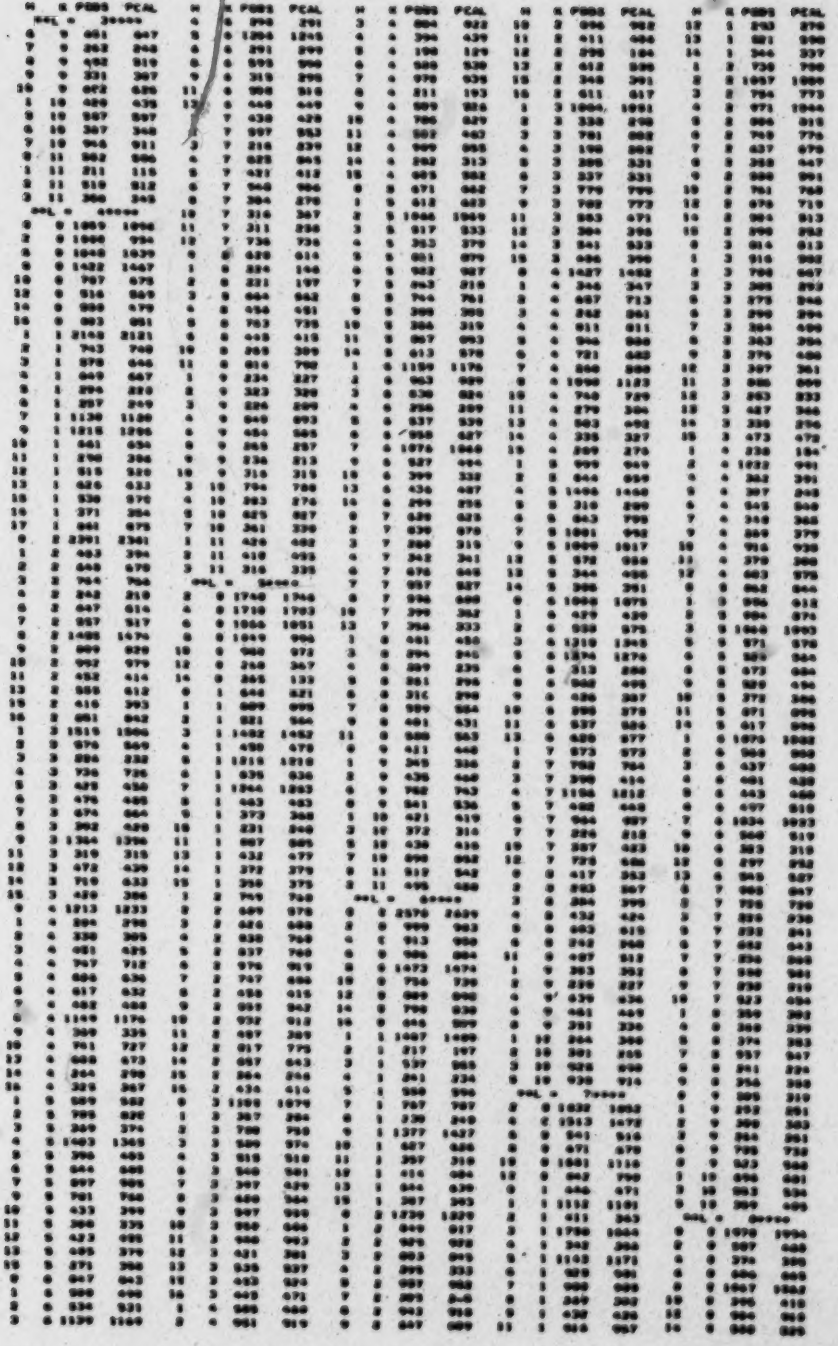


Table 28 continued

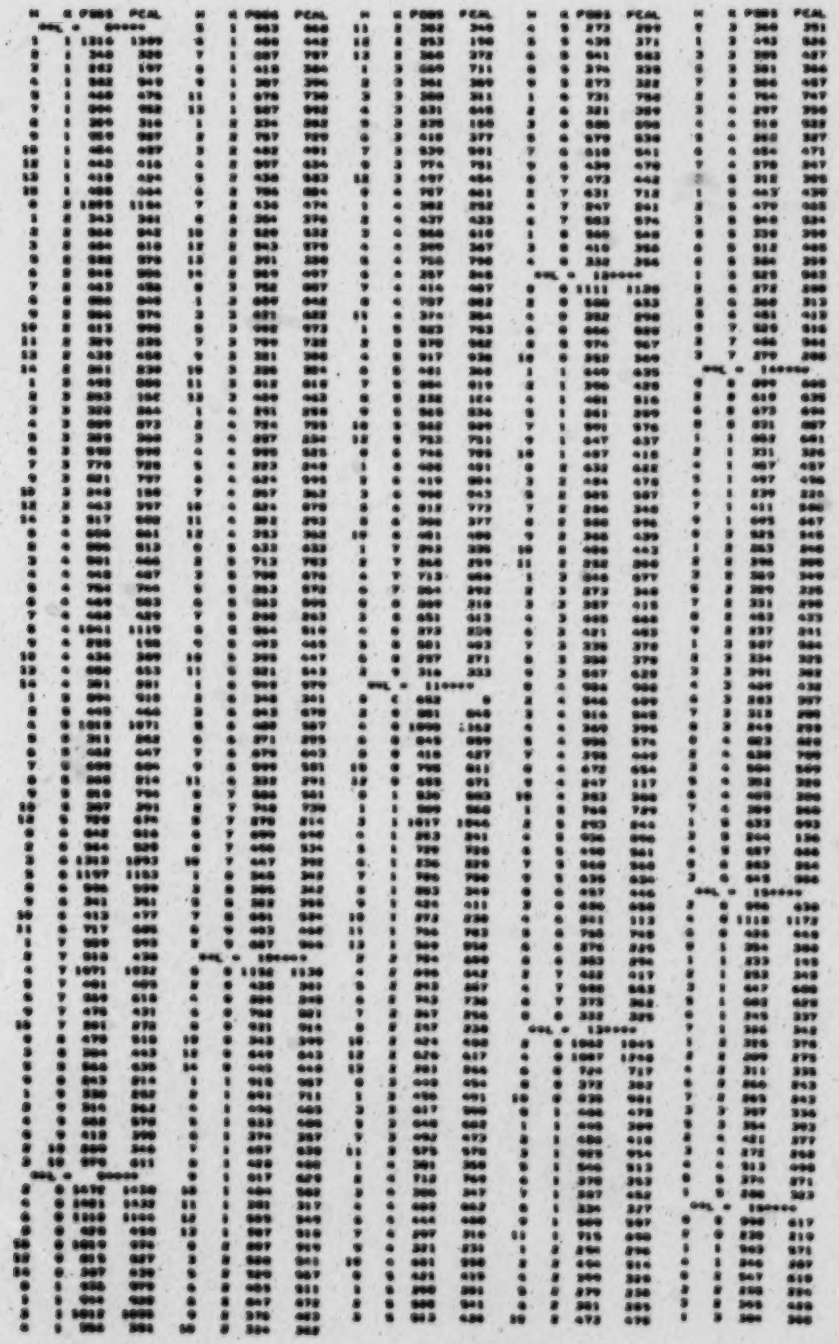


Table 29

Atomic Coordinates and Isotropic Temperature Factors for the Unique Contents of the Unit Cell

Name	x	y	z	B *
Rh	0.06304(5)	0.02892(9)	0.2500(0)	2.38
Cl	-0.0508(2)	0.0726(3)	0.2088(3)	3.88
P1	0.0800(2)	0.2085(3)	0.2555(4)	2.91
P2	0.1723(2)	-0.0199(3)	0.2607(4)	2.81
P3	0.0154(2)	-0.1362(3)	0.2757(2)	2.71

* These values are equivalent isotropic temperature factors corresponding to the anisotropic temperature factors given in table 30

(Table continued)

Table 29 continued

(a) Phenyl Carbon Rigid Bodies

Name	x	y	z	B
C111	0.0247(6)	0.273(1)	0.3240(6)	3.0(4)
C112	0.0372(5)	0.377(1)	0.3439(5)	7.6(7)
C113	-0.0054(7)	0.4268(7)	0.3945(8)	8.4(7)
C114	-0.0605(6)	0.373(1)	0.4253(6)	5.8(5)
C115	-0.0730(5)	0.268(1)	0.4054(5)	4.8(4)
C116	-0.0305(7)	0.2184(7)	0.3548(8)	4.0(4)
D	0.318(8)	$x^{1\ddagger}$	-0.0179(4)	
E	0.669(8)	$y^{1\ddagger}$	0.3226(7)	
F	5.783(9)	$z^{1\ddagger}$	0.3746(4)	
C121	0.0606(6)	0.278(1)	0.1699(6)	3.4(4)
C122	0.0657(6)	0.2186(7)	0.1059(8)	3.9(4)
C123	0.0549(7)	0.266(1)	0.0379(6)	6.2(5)
C124	0.0389(6)	0.373(1)	0.0339(6)	5.7(5)
C125	0.0338(6)	0.4322(7)	0.0979(8)	6.4(6)
C126	0.0446(7)	0.385(1)	0.1659(6)	5.6(6)
D	6.061(7)	x^{1}	0.0497(4)	
E	1.632(8)	y^{1}	0.3254(6)	
F	3.599(8)	z^{1}	0.1019(5)	
C131	0.1620(8)	0.2692(8)	0.2818(9)	2.6(4)
C132	0.201(1)	0.3252(9)	0.2308(6)	3.2(4)
C133	0.2614(8)	0.3746(8)	0.253(1)	5.3(4)

(Table continued)

Table 29 continued

Name	x	y	z	B
C134	0.2830(8)	0.3680(8)	0.3254(9)	4.6(5)
C135	0.244(1)	0.3119(9)	0.3763(6)	6.1(5)
C136	0.1837(8)	0.2625(8)	0.355(1)	5.7(5)
D	0.979(6)	x^1	0.2225(4)	
E	1.97(1)	y^1	0.3186(5)	
F	5.34(1)	z^1	0.3036(4)	
C211	0.2396(6)	0.0633(8)	0.220(1)	2.9(4)
C212	0.232(1)	0.0852(8)	0.1451(7)	3.8(4)
C213	0.282(1)	0.1424(8)	0.1081(8)	5.7(5)
C214	0.3401(6)	0.1777(8)	0.146(1)	4.8(5)
C215	0.348(1)	0.1559(8)	0.2201(7)	3.1(4)
C216	0.298(1)	0.0987(8)	0.2571(8)	3.5(3)
D	1.017(6)	x^1	0.2899(4)	
E	2.01(1)	y^1	0.1205(5)	
F	4.58(1)	z^1	0.1826(4)	
C221	0.1885(8)	-0.1394(8)	0.2047(9)	2.9(4)
C222	0.1481(7)	-0.1499(9)	0.1420(6)	4.4(5)
C223	0.1593(9)	-0.233(1)	0.0939(5)	6.3(5)
C224	0.2109(8)	-0.3064(8)	0.1085(9)	6.5(5)
C225	0.2513(7)	-0.2959(9)	0.1712(6)	5.9(5)
C226	0.2401(9)	-0.212(1)	0.2193(5)	5.0(5)
D	2.548(7)	x^1	0.1997(4)	
E	2.239(9)	y^1	-0.2229(6)	
F	4.305(9)	z^1	0.1566(4)	

(Table continued)

Table 29 continued

Name	x	y	z	B
C231	0.204(2)	-0.044(1)	0.356(1)	3.7(4)
C232	0.268(1)	-0.087(1)	0.372(1)	7.3(6)
C233	0.2879(6)	-0.104(1)	0.445(2)	7.8(6)
C234	0.244(2)	-0.076(1)	0.502(1)	6.5(6)
C235	0.180(1)	-0.032(1)	0.486(1)	7.2(6)
C236	0.1601(6)	-0.016(1)	0.413(2)	5.1(5)
D	1.986(8)	x^1	0.2240(5)	
E	1.51(2)	y^1	-0.0599(6)	
F	5.91(2)	z^1	0.4289(5)	
C311	-0.0533(6)	-0.1085(9)	0.3436(8)	2.9(4)
C312	-0.0379(5)	-0.0402(8)	0.4012(5)	3.5(4)
C313	-0.0876(8)	-0.0167(8)	0.4537(7)	4.5(4)
C314	-0.1527(6)	-0.0613(9)	0.4486(8)	4.8(5)
C315	-0.1682(5)	-0.1295(8)	0.3911(5)	4.2(4)
C316	-0.1185(8)	-0.1531(8)	0.3385(7)	3.6(4)
D	0.887(7)	x^1	-0.1030(4)	
E	0.51(1)	y^1	-0.0849(5)	
F	5.94(1)	z^1	0.3961(4)	
C321	0.0649(6)	-0.2422(8)	0.3208(8)	3.6(4)
C322	0.0965(9)	-0.320(1)	0.2785(4)	3.6(4)
C323	0.1365(6)	-0.3968(8)	0.3121(8)	4.8(5)
C324	0.1449(6)	-0.3965(8)	0.3880(8)	4.7(5)

(Table continued)

Table 29 continued

Name	x	y	z	B
C325	0.1133(9)	-0.319(1)	0.4304(4)	6.2(5)
C326	0.0733(6)	-0.2419(8)	0.3968(8)	4.6(4)
D	2.521(7)	x^1	0.1049(3)	
E	1.691(9)	y^1	-0.3194(5)	
F	5.239(9)	z^1	0.3544(4)	
C331	-0.0278(6)	-0.212(1)	0.2037(6)	3.9(4)
C332	-0.0329(6)	-0.1672(7)	0.1340(9)	5.0(5)
C333	-0.0650(7)	-0.222(1)	0.0775(6)	8.0(6)
C334	-0.0921(6)	-0.322(1)	0.0906(6)	7.7(6)
C335	-0.0870(6)	-0.3669(7)	0.1603(9)	5.5(5)
C336	-0.0549(7)	-0.312(1)	0.2168(6)	4.4(4)
D	3.566(7)	x^1	-0.0599(4)	
E	1.851(8)	y^1	-0.2671(7)	
F	3.725(9)	z^1	0.1471(5)	

^{1} These values are the coordinates of the ring center of gravity.

(Table continued)

Table 29 continued

(b) Phenyl Hydrogen Rigid Bodies

Name	x	y	z	B
H112	0.077	0.416	0.322	8.3
H113	0.004	0.501	0.410	9.4
H114	-0.091	0.408	0.462	6.5
H115	-0.112	0.229	0.427	5.2
H116	-0.039	0.144	0.340	4.2
D	0.318			
E	0.669			
F	6.830			
H122	0.077	0.142	0.109	4.2
H123	0.059	0.223	-0.008	6.7
H124	0.031	0.407	-0.015	6.4
H125	0.022	0.509	0.095	6.9
H126	0.041	0.427	0.212	6.3
D	6.061			
E	1.632			
F	4.646			
H132	0.186	0.331	0.179	3.5
H133	0.290	0.416	0.218	5.9
H134	0.326	0.403	0.343	5.9
H135	0.259	0.305	0.429	6.6
H136	0.155	0.221	0.391	6.3

(Table continued)

Table 29 continued

Name	x	y	z	B
D	0.979			
E	1.97			
F	6.39			
H212	0.190	0.060	0.118	4.0
H213	0.277	0.158	0.054	6.0
H214	0.376	0.219	0.119	5.2
H215	0.390	0.181	0.247	3.3
H216	0.303	0.083	0.310	4.0
D	1.017			
E	2.01			
F	5.62			
H222	0.111	-0.097	0.132	4.8
H223	0.130	-0.241	0.049	6.7
H224	0.219	-0.366	0.074	7.1
H225	0.288	-0.349	0.181	6.9
H226	0.269	-0.205	0.264	5.5
D	2.548			
E	2.239			
F	5.350			
H232	0.300	-0.107	0.331	7.5
H233	0.334	-0.135	0.457	8.6
H234	0.257	-0.087	0.554	7.1

(Table continued)

Table 29 continued

Name	x	y	z	B
H235	0.148	-0.012	0.527	7.6
H236	0.114	0.015	0.402	5.6
D	1.986			
E	1.51			
F	6.96			
H312	0.009	-0.008	0.405	3.8
H313	-0.077	0.032	0.495	4.7
H314	-0.188	-0.045	0.486	5.1
H315	-0.215	-0.162	0.387	4.8
H316	-0.130	-0.202	0.297	4.0
D	0.887			
E	0.51			
F	6.99			
H322	0.091	-0.321	0.224	4.0
H323	0.160	-0.453	0.283	5.2
H324	0.173	-0.451	0.414	5.2
H325	0.119	-0.318	0.486	6.7
H326	0.050	-0.186	0.427	5.1
D	2.521			
E	1.691			
F	6.286			

(Table continued)

Table 29 continued

Name	x	y	z	B
H332	-0.013	-0.096	0.124	5.6
H333	-0.069	-0.191	0.027	9.0
H334	-0.115	-0.363	0.050	8.5
H335	-0.107	-0.439	0.170	6.4
H336	-0.051	-0.343	0.267	4.7
D	3.566			
E	1.851			
F	4.772			

Table 30

Anisotropic Temperature Factors ($\AA^2 \times 10^3$)

Name	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Rh	24.6(6)	27.3(6)	38.6(7)	-0.4(6)	0(1)	0(1)
Cl	30(3)	48(3)	69(3)	1(2)	-11(3)	6(2)
P1	32(3)	34(2)	45(3)	-1(2)	- 3(4)	-5(4)
P2	26(2)	35(2)	46(4)	0(2)	3(3)	-3(4)
P3	34(3)	25(2)	44(4)	-3(2)	0(3)	0(2)

Table 31

Selected Interatomic Distances

Atom 1	Atom 2	Distance (Å)	
Rh	Cℓ	2.404(4)	2.416(4)*
Rh	P1	2.304(4)	2.307(4)*
Rh	P2	2.225(4)	2.228(4)*
Rh	P3	2.338(4)	2.341(4)*
P1	C111	1.84(1)	
P1	C121	1.83(1)	
P1	C131	1.836(9)	
P2	C211	1.841(9)	
P2	C221	1.85(1)	
P2	C231	1.87(1)	
P3	C311	1.856(9)	
P3	C321	1.847(9)	
P3	C331	1.83(1)	

* value corrected for riding

Table 32

Selected Interatomic Angles

Atom 1	Atom 2	Atom 3	Angle (°)
P1	Rh	P2	97.7(1)
P1	Rh	P3	159.1(2)
P1	Rh	Cℓ	85.3(1)
P1	Rh	H222	122.9
P2	Rh	P3	96.4(2)
P2	Rh	Cℓ	166.7(2)
P2	Rh	H222	66.1
P3	Rh	Cℓ	84.5(1)
P3	Rh	H122	77.1
Cℓ	Rh	H122	101.3
Rh	P1	C111	112.5(5)
Rh	P1	C121	114.3(5)
Rh	P1	C131	123.4(4)
Rh	P2	C211	119.0(4)
Rh	P2	C221	109.9(5)
Rh	P2	C231	116.4(5)
Rh	P3	C311	104.4(4)
Rh	P3	C321	122.3(4)
Rh	P3	C331	120.6(5)
P1	C111	C114	178.7(8)
P1	C121	C124	175.1(8)
P1	C131	C134	177.3(6)

(Table continued)

Table 32

Selected Interatomic Angles

Atom 1	Atom 2	Atom 3	Angle (°)
P1	Rh	P2	97.7(1)
P1	Rh	P3	159.1(2)
P1	Rh	Cℓ	85.3(1)
P1	Rh	H222	122.9
P2	Rh	P3	96.4(2)
P2	Rh	Cℓ	166.7(2)
P2	Rh	H222	66.1
P3	Rh	Cℓ	84.5(1)
P3	Rh	H122	77.1
Cℓ	Rh	H122	101.3
Rh	P1	C111	112.5(5)
Rh	P1	C121	114.3(5)
Rh	P1	C131	123.4(4)
Rh	P2	C211	119.0(4)
Rh	P2	C221	109.9(5)
Rh	P2	C231	116.4(5)
Rh	P3	C311	104.4(4)
Rh	P3	C321	122.3(4)
Rh	P3	C331	120.6(5)
P1	C111	C114	178.7(8)
P1	C121	C124	175.1(8)
P1	C131	C134	177.3(6)

(Table continued)

Table 32 continued

Atom 1	Atom 2	Atom 3	Angle (°)
P2	C211	C214	174.6(7)
P2	C221	C224	174.3(8)
P2	C231	C234	176.4(9)
P3	C311	C314	177.6(7)
P3	C321	C324	177.4(7)
P3	C331	C334	178.1(9)
C111	P1	C121	104.1(5)
C111	P1	C131	98.5(6)
C121	P1	C131	101.5(6)
C211	P2	C221	97.2(6)
C211	P2	C231	103.5(6)
C221	P2	C231	108.9(6)
C311	P3	C321	102.6(5)
C311	P3	C331	104.2(6)
C321	P3	C331	100.2(6)

Table 33

Selected Intermolecular Contacts

Atom 1	Atom 2	Symmetry Operation (on atom 2)	Distance (Å)
H112	H323	x,y+1,z	2.41
H113	H124	$\bar{x},\bar{y}$+1,1/2+z	1.92
H123	H326	$\bar{x},\bar{y}$,1/2+z-1	2.48
H212	H314	$\bar{x},\bar{y}$,1/2+z-1	2.40
H213	H325	1/2-x,1/2+y,1/2+z-1	2.41
H214	H325	1/2-x,1/2+y,1/2+z-1	2.47

Table 34

Selected Intramolecular Non-Bonded Contacts

Atom 1	Atom	Distance (Å)
Rh	H222	2.84
Rh	H236	2.94
Rh	H122	2.96
Rh	H116	2.96
P1	Cℓ	3.190(6)
P3	Cℓ	3.188(6)
P1	P2	3.411(5)
P2	P3	3.404(6)
H112	H126	2.12
H226	H232	1.84
H236	H312	2.07
C131	C211	3.22(1)
C133	C215	3.30(1)
C221	C322	3.20(1)
C226	C322	3.29(1)
C236	C326	3.34(1)

Fig. 11

View Perpendicular to the P1-P2-P3 Plane

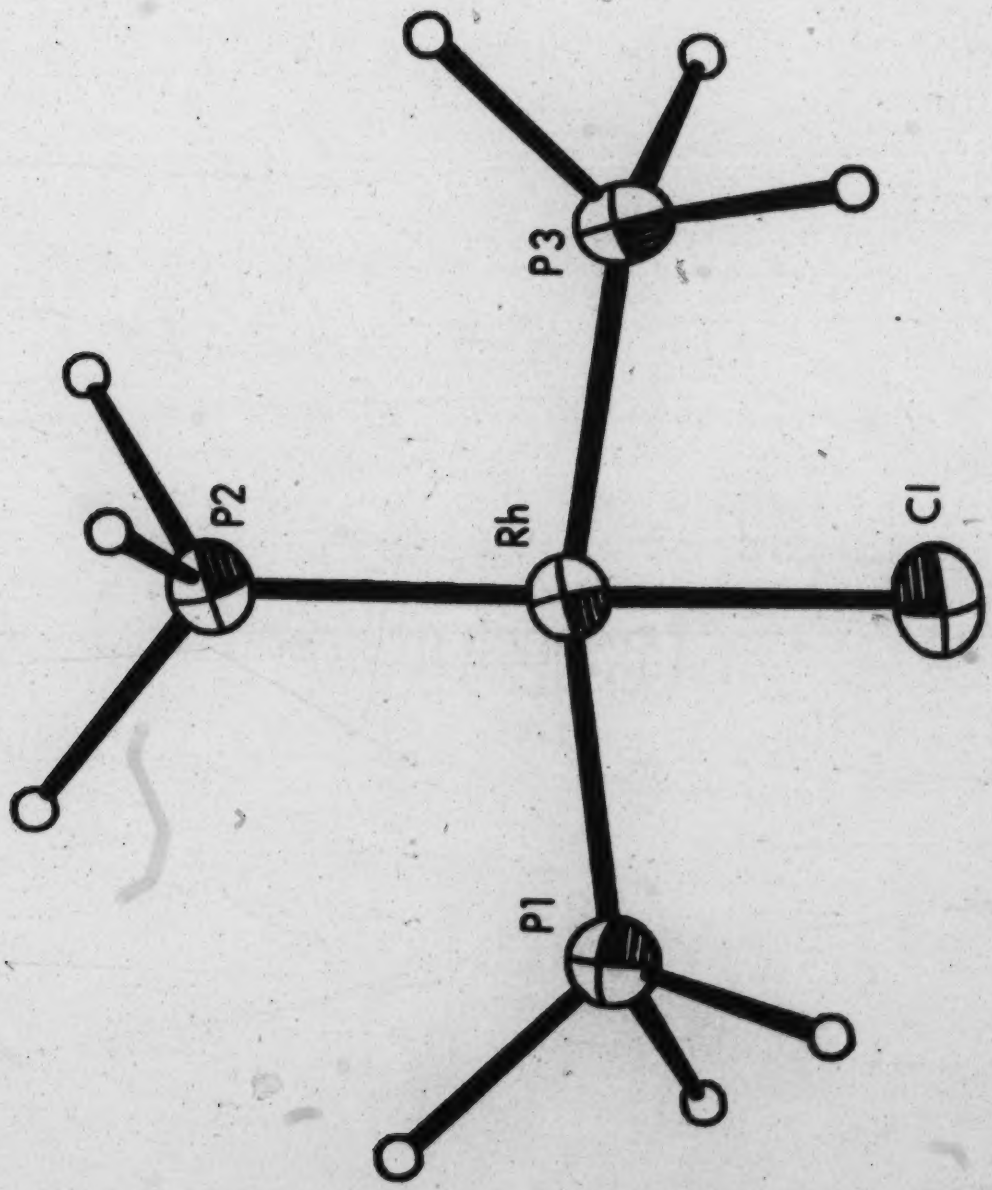


Fig. 12

Central Geometry Viewed down P1-P3 Direction

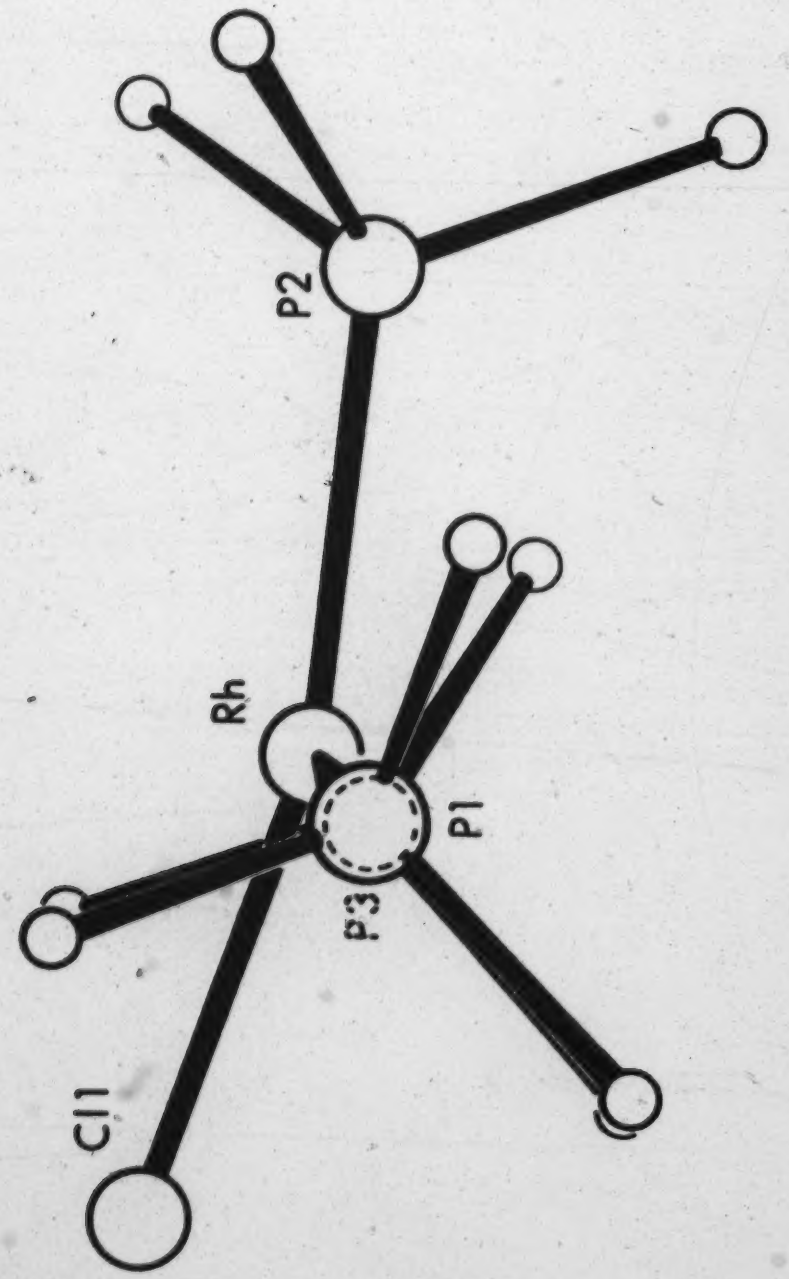
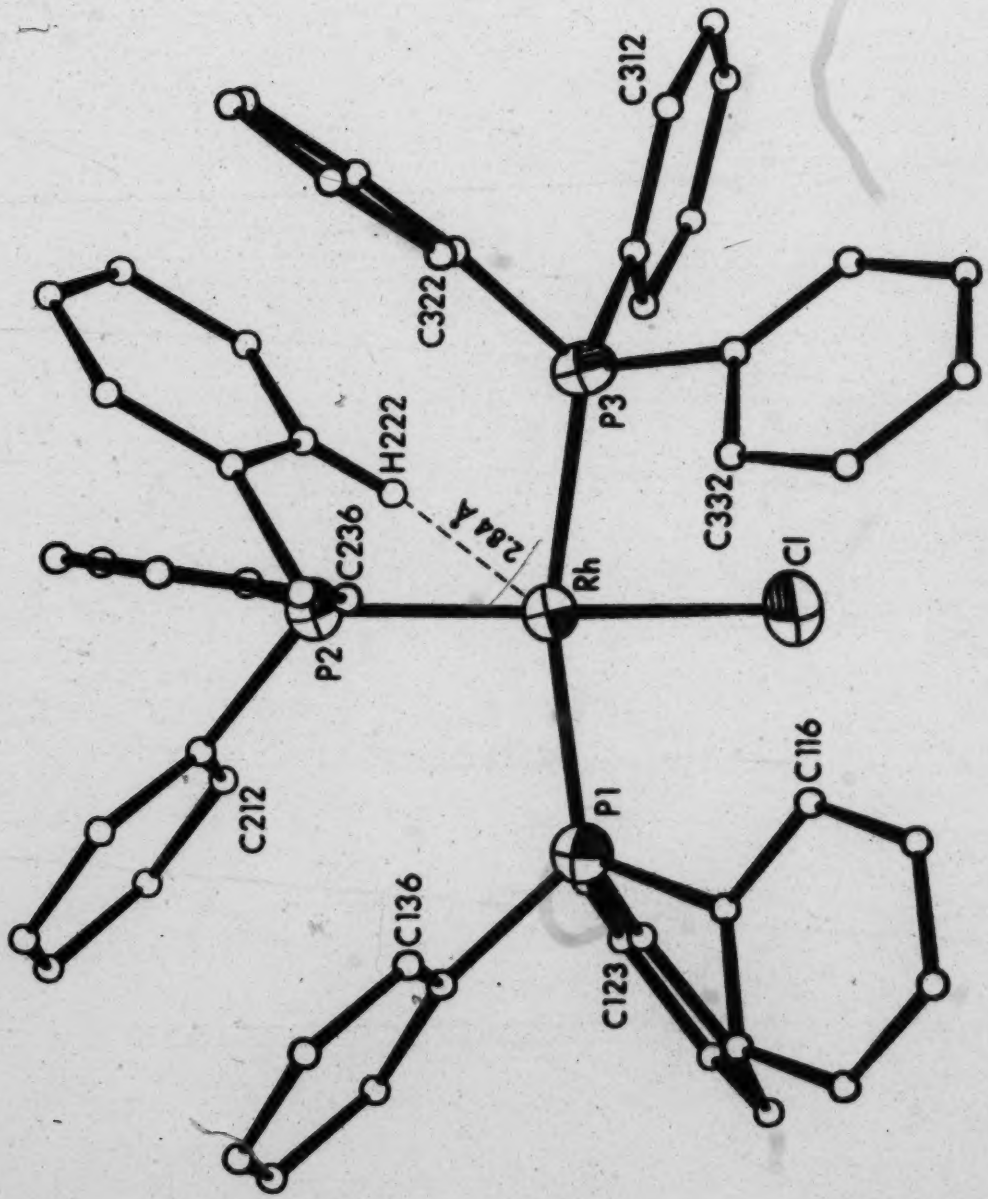


Fig. 13

A General View of $[RhCl(P(C_6H_5)_3)_3]$ (Orange Form)



Discussion

To a first approximation the coordination of the rhodium atom (Fig. 11) is square planar but there is a marked distortion towards tetrahedral geometry as emphasized by Fig. 12 and the angles Cl-Rh-P2 and P1-Rh-P3 of 166.7(2)° and 159.1(2)° respectively. The latter angle cannot be interpreted simply as being due to the distortion towards a tetrahedral geometry since it contains a significant contribution from a bending of P1-Rh-P3 within the mean molecular plane of the complex. The distortions from square planar coordination are explained by the bulkiness of the triphenylphosphine ligands *(vide infra)*.

The phosphorus atoms can be grouped chemically into two categories, (1) one pair mutually *trans* and *cis* to the chlorine atom, and (2) the unique phosphorus *trans* to chlorine. For this latter phosphorus, the rhodium-phosphorus bond length is 2.228(4) Å which is significantly shorter than the other two bond lengths (Rh-P1, 2.307(4), Rh-P3, 2.341(4) Å) between rhodium and the mutually *trans* phosphorus atoms (Δ/σ: 14 and 19 respectively). This pattern of rhodium-phosphorus bond lengths is consistent with the π-acidity and thus *trans* effect of phosphorus being greater than that of chlorine [137-141]. The difference between the chemically equivalent rhodium-phosphorus bond lengths appears to be statistically significant (Δ/σ,6)

and may reflect differences in intra ligand contacts. The difference may not be significant in that the standard deviations as derived must underestimate the true values if systematic errors are present.

The average phosphorus-carbon bond length in this structure is 1.844 Å and is somewhat longer than the value observed for triphenylphosphine [129] and its typical metal complexes [17,18] (~1.83Å). This increase appears to be correlated to the short rhodium-phosphorus bonds. If the phosphorus-carbon bond lengths are sorted according to the phosphorus atom then the bonds involving P1 and P3 average 1.838 Å while those involving P2 average 1.855 Å. An analysis of the six phosphorus-carbon bonds involving P1 and P3 shows that they are consistent with a standard deviation of 0.010 Å which is in remarkable agreement with the standard deviations derived *via* the least squares refinement and ORFFE II. The P2-carbon distances show a maximum deviation from their mean 1.6σ. The difference between the group averages is interesting but not acceptable as statistically significant by normal conservative crystallographic criteria. It was this feature which lead to the redetermination of the structure of the red form (Chapter VI) since it might provide independent evidence of the observed trend and averaging the values of both structures might produce a significant variation in distances.

The rhodium-chlorine bond length agrees well with those observed for the dioxygen derivatives described in Chapters III and IV but appears to be rather longer than the values as reported by Mason *et al.*,[138] for the red form of $RhCl(P(C_6H_5)_3)_3$, (2.373(8), 2.381[140] Å) and $RhCl(C_2F_4)(P(C_6H_5)_3)_2$, (2.375(8) Å). This topic is discussed in more detail in Chapter VI.

The final structural detail to be discussed is the close rhodium-H222 contact of 2.84 Å which is evident in Fig. 13. This close contact could result from (1) natural attraction of the hydrogen for the rhodium atom, or (2) a repulsion elsewhere in the molecule[139]. Table 33 contains all important intramolecular non-bonded contacts. In this Table if one ignores contacts between carbon atoms of the type (M11),(M21),(M31) then there are surprisingly few contacts between phenyl groups that are significantly less than the sum of the van der Waals radii. These contacts are: H112-H126, 2.12 Å: H226-H232, 1.84 Å; H236-H312, 2.07 Å; C131-C211, 3.22(1) Å; C133-C215, 3.30(1) Å; C221-C322, 3.20(1) Å; C226-C322, 3.29 Å; C236-C326, 3.34 Å. From these contacts it is obvious that phenyl group 22 is repelled by H232 and C322 into close contact with the rhodium atom i.e. the short rhodium hydrogen contact cannot be treated as representing an attractive force. Rather it represents a balance of repulsive forces. There is also a larger number of

repulsions involving the atoms of the phenyl groups attached to P3 relative to the number of repulsions involving the atoms of the phenyl rings attached to P1. Thus one could explain the slight increase of bond length for Rh-P3 when compared to Rh-P1. It is highly doubtful that the interligand repulsions lead to the apparently abnormal phosphorus-carbon bond lengths in this structure. This view is discussed further in Chapter VI. Intermolecular contacts are listed in Table 32. Only one of these contacts is abnormally short *viz*. H113 at x,y,z to H124 at $\bar{x}$, 1-y, 1/2+z of 1.92 Å. All other contacts are equal to or greater than the sum of the van der Waals radii and further discussion is not warranted.

CHAPTER VI

The Crystal and Molecular Structures of the Red Form of $RhCl(P(C_6H_5)_3)_3$.

Experimental

Dark red crystals of the compound were examined under a polarizing microscope and found to be chunky, capped prisms, with no sign of twinning being evident. A crystal was mounted on the end of a thin glass fibre and a Laué photograph taken. Again no crystal defects were noticed and the crystal appeared to be suitable for a diffraction study. Preliminary Weissenberg and precession photographs indicated that the compound crystallized in the orthorhombic crystal system (Laué symmetry mmm). The systematic absences ($0k\ell$, $k + \ell = 2n + 1$; $h0\ell$, $h = 2n + 1$) were consistent with the spacegroups $Pna2_1$ or Pnam.

Precise lattice parameters were obtained from a least squares refinement using 2θ values of 18 accurately centered high angle reflections ($CuK\alpha_1$ 1.54051 Å) as: a, 32.96(1); b, 12.271(2); C, 11.013(1) Å. All reflections used showed resolvable splitting of the α_1/α_2 peaks. The density of the compound was measured by flotation in aqueous potassium iodide solution as ρ_{obs} = 1.382 g-cm^3, a value in good agreement with that calculated using precise lattice parameters, ρ_{calc} =

1.379 g-cm^{-3} (for 4 molecules per unit cell).

Intensity data were collected on a Picker manual diffractometer with the crystal "b" axis aligned coincident with the diffractometer ϕ axis. Copper $k\bar{\alpha}$ X-radiation was used with a graphite monochromator (002 reflecting plane) and a 2° takeoff angle. Diffractometer settings were calculated using the programme MIXG2 and the high intensity axial peaks were scanned at expanded chart speeds to detect twinning or unusual reflection shape. No unusual effects were found. Each reflection was scanned from $(2\theta - 1)°$ to $(2\theta + 1)°$ in 1 minute and 20 second stationary background counts were taken at the limits of the coupled $\omega/2\theta$ scan. The total background counts were calculated from a linear interpolation of the two stationary counts. Data were only measured to 90° in 2θ because of the rapid decrease in intensities with increasing 2θ as observed in the preliminary photographic study. During the data collection 5 reflections were measured at 8 hour intervals to check against crystal misalignment and/or decomposition. No significant changes in these intensities were found throughout the entire data collection. A total of 2221 reflections were measured and of this number 1469 were statistically reliable using the criterion $I \leq 3\sigma$ for rejection. Reflections having a maximum count rate in excess of 10^4 counts-sec^{-1} (and thus

greater than the linear response of the scintillation counter) were recollected at the end of the initial data collection at reduced voltages and scaled into the data by comparison with the other reflections of lower intensity, recollected under the same conditions. The 0k0 reflections were measured at 10° intervals in ϕ to provide experimental verification of absorption corrections.

The crystal faces were identified as members of the forms {100}, {210}, {201} and the crystal was removed from the diffractometer. The crystal dimensions (0.17 x 0.21 x 0.14 mm) were measured under a calibrated microscope. These values were used to make an absorption correction ($\mu_{K\bar{\alpha}} = 47.6\ cm^{-1}$) and the data for different ϕ values after correction for absorption were consistent within 5%. Transmission factors varied from 0.683 to 0.566. Reflection data were corrected for Lorentz and polarization effects and the structure amplitudes with their respective standard deviations calculated using an uncertainty factor of 0.03. Only the significant data were used in the structure solution and refinement.

Solution of Structure and Refinement

A Patterson map was calculated and the molecule was assumed to have the more general space group $Pna2_1$

for reasons outlined in Chapter V. The Harker lines gave peaks representing the rhodium-rhodium intermolecular vectors and the rhodium "x" and "y" coordinates were obtained. The "z" coordinate of the rhodium atom was set at 0.25 to fix the origin in this direction. The atomic coordinates of the chlorine atom were found from the intramolecular vectors and checked with the Harker line peaks for this atom (see Table 35). The remaining atoms were identified in a series of electron density difference maps as indicated in Table 36.

The rigid body description for the carbon atoms of the phenyl groups was used to minimize the number of parameters. The atomic scattering factors for the rhodium, chlorine, phosphorus and carbon atoms were for neutral species. These were derived from Cromer's coefficients [111] and included (for rhodium, chlorine and phosphorus) the real and imaginary terms for anomalous dispersion. Hydrogen atoms were added to the refinement at their calculated positions with carbon-hydrogen bond lengths of 1.0 Å and isotropic temperature factors 10% greater than those of the carbon atoms to which they were attached. Hydrogen scattering factors were those of Mason and Robertson [113].

Refinement of the completed structure was routine (Table 37) except for problems caused by an error

in the refinement programme that was specific to noncentrosymmetric space groups. Elimination of this error allowed the structure to refine to convergence. As mentioned in Chapter V two solutions must be tested for this spacegroup when anomalous scattering is considered. When the molecule was reflected through the "xy" plane a Hamilton test showed that the new model was preferred at better than the 99.5% confidence level.

At convergence (estimated standard deviation of an observation of unit weight = 1.595; maximum shift/σ = 0.02; R_1 = 0.042; R_2 = 0.045) a final electron density difference map was calculated and the correlation matrix printed. Examination of the electron density map showed the largest positive and negative peaks (0.38 e.$\mathring{A}^{-3}$ and -0.20 e.$\mathring{A}^{-3}$; cf. carbon ~3e.$\mathring{A}^{-3}$) to be situated near phenyl groups. The correlation matrix showed high correlations between some phenyl carbon temperature factors, but all coordinate interactions were less than 0.18.

All interatomic bond lengths, inter- and intramolecular contacts (with their angles and standard deviations) to a distance of 3.5 $\mathring{A}$ were calculated using ORFFE II. Bond lengths involving the rhodium atom were also calculated to include a correction for thermal motion assuming the lighter atoms to ride on the heavier rhodium atom.

Table 35

Assignment of Patterson Map Peaks

Peak Coordinates u, v, w	Rel. Height (origin=999)	Assignment	Calc. Height	Calc. Coordinates (from Solution)
0.504, 0.204, 0.000	295	$1/2, 1/2-2y_a, 0$	198	0.500, 0.256, 0.000
0.270, 0.504, 0.494	285	$1/2-2x_a, 1/2, 1/2$	198	0.274, 0.500, 0.500
0.225, 0.240, 0.494	167	$2x_a, 2y_a, 1/2$	99	0.226, 0.244, 0.500
0.347, 0.504, 0.494	78	$1/2-2x_b, 1/2, 1/2$	28	0.346, 0.500, 0.500
0.504, 0.312, 0.000	60	$1/2, 1/2-2y_b, 0$	28	0.500, 0.322, 0.000
0.148, 0.176, 0.494	40	$2x_b, 2y_b, 1/2$	14	0.154, 0.178. 0.500
0.036, 0.020, 0.182	43	$x_a-x_b, y_a-y_b, z_a-z_b$	37	0.036, 0.033, 0.184
0.309, 0.480, 0.312	34	$1/2-x_a-x_b, 1/2-y_a+y_b, 1/2-z_a+z_b$	37	0.310, 0.467, 0.316
0.462, 0.288, 0.182	31	$1/2-x_a+x_b, 1/2-y_a-y_b, z_a-z_b$	37	0.464, 0.289, 0.184
0.193, 0.216, 0.312	29	$x_a+x_b, y_a+y_b, 1/2-z_a+z_b$	37	0.190, 0.211, 0.316

Assignment Results	x	y	z
a = Rh	0.113	0.122	-0.250
b = Cl	0.077	0.089	-0.434

Table 36

Structure Solution Sequence

Refinement Cycle	Atoms used in Phasing	R_1	Atoms Located in Diff. Map
1	Rh,Cl	0.427	P1,P2,P3
2	Rh,Cl,P1,P2,P3	0.326	
3	.. ..	0.281	C111-C116,C131-C136,C221-C226, C331-C336
4	Rh,Cl,P1,P2,P3,C111-C116, C131-C136,C221-C226,C331-C336	0.262	
5	.. ..	0.245	C121-C126,C211-C216,C231-C236, C311-C316,C321-C326

Table 37

Refinement Sequence for Model

Refinement Cycle		R_1	R_2
6	All atoms except hydrogens included, temperature factors held constant (B:Rh, 2.5; Cl, 2.5; P, 3.0; C, 5.0)	0.201	0.220
7	.. ..	0.172	0.193
8	temperature factors refined	0.147	0.164
9	.. ..	0.112	0.129
10	anomalous dispersion correction applied	0.097	0.107
11	central atoms given anisotropic temperature factors	0.079	0.086
12	hydrogen atoms included	0.072	0.078
13	error in refinement programme corrected	0.047	0.056
14	origin molecule reflected through "xy" plane	0.044	0.047
15	.. ..	0.042	0.044

Results

The observed and calculated structure amplitudes ($|F_o|$) and $|F_c|$ respectively) are listed in Table 38. Table 39 gives the atomic coordinates of all atoms with the anisotropic thermal parameters of the central atoms being included in Table 40. The interatomic angles and distances are given in Tables 41 and 42 respectively with the inter- and intramolecular non-bonded contacts being listed in Tables 43 and 44. The standard deviations of the least significant digit are included in parentheses.

Fig. 14 shows the general geometry of the molecule whilst Figs. 15 and 16 show views down the P1-P3 direction and perpendicular to the P1-P2-P3 plane.

Table 38

Observed and Calculated Structure Amplitudes (electronsx10)

H	K	FOBS	FCAL	H	K	FOBS	FCAL	H	K	FOBS	FCAL	H	K	FOBS	FCAL	H	K	FOBS	FCAL
L = 0**				12	3	571	583	17	6	484	481	5	1	343	335	4	4	445	465
2	0	364	361	13	3	381	384	19	6	728	750	6	1	1414	1432	5	4	301	278
4	0	2344	2418	15	3	364	371	21	6	303	257	7	1	2074	2034	6	4	1142	1158
6	0	393	394	16	3	773	644	23	6	578	568	8	1	672	678	7	4	1486	1484
8	0	980	987	17	3	484	480	25	6	582	594	9	1	1347	1362	8	4	1325	1317
10	0	1248	1267	19	3	870	808	2	7	938	960	10	1	907	912	9	4	497	498
12	0	422	457	20	3	570	559	3	7	422	446	11	1	1325	1343	10	4	941	932
14	0	468	497	21	3	262	337	4	7	1114	1162	12	1	741	769	11	4	571	548
16	0	744	720	23	3	254	276	5	7	780	828	13	1	264	300	12	4	958	893
18	0	851	777	24	3	398	421	6	7	638	785	14	1	830	863	13	4	284	313
20	0	903	1071	25	3	279	315	7	7	638	568	15	1	893	965	14	4	485	477
22	0	1282	1366	26	3	391	401	8	7	965	919	17	1	701	691	15	4	527	499
24	0	563	529	27	3	364	351	9	7	328	294	18	1	958	938	16	4	1006	1041
26	0	1191	1224	0	4	1549	1550	10	7	703	766	19	1	809	883	17	4	369	395
28	0	702	667	1	4	415	424	12	7	419	464	20	1	493	569	20	4	917	889
30	0	452	485	2	4	385	386	13	7	326	365	21	1	568	585	21	4	264	301
1	1	1531	1531	3	4	303	318	14	7	486	443	22	1	786	788	23	4	412	414
2	1	1660	1670	4	4	2986	3102	15	7	600	627	23	1	609	613	24	4	635	660
3	1	1508	1588	5	4	1410	1431	17	7	286	323	25	1	319	348	25	4	276	227
4	1	669	694	6	4	265	341	20	7	315	335	26	1	502	482	27	4	366	376
5	1	748	791	7	4	617	605	23	7	481	429	27	1	372	397	28	4	639	684
6	1	779	662	8	4	1155	1135	0	8	967	941	28	1	560	589	0	5	1125	1139
7	1	2682	2709	9	4	1020	995	2	8	365	337	29	1	478	477	1	5	1209	1241
8	1	2049	2015	10	4	329	345	4	8	857	888	1	2	410	427	2	5	284	308
9	1	681	669	11	4	390	360	6	8	642	687	2	2	577	584	3	5	1291	1294
10	1	240	229	12	4	485	468	7	8	367	304	3	2	553	562	4	5	1140	1144
11	1	827	833	13	4	807	785	8	8	504	481	4	2	675	658	5	5	303	276
12	1	880	876	14	4	880	889	10	8	801	469	5	2	989	983	7	5	863	881
13	1	1006	1025	15	4	364	392	11	8	716	760	6	2	439	408	8	5	747	756
14	1	466	398	17	4	675	721	14	8	330	335	7	2	733	730	9	5	684	644
15	1	212	218	18	4	1024	1105	18	8	390	417	9	2	1183	1170	10	5	488	489
16	1	381	362	22	4	794	786	19	8	282	223	10	2	622	610	11	5	1113	1126
17	1	1065	1112	25	4	431	412	6	9	313	285	11	2	814	843	12	5	890	933
18	1	658	614	26	4	569	502	8	9	447	403	12	2	406	433	13	5	197	130
19	1	677	715	27	4	322	386	6	9	770	768	13	2	1133	1119	14	5	968	1003
20	1	976	1011	28	4	256	232	7	9	262	255	14	2	767	761	15	5	690	668
21	1	497	498	1	5	1430	1374	9	9	1032	1065	15	2	1340	1347	16	5	310	332
22	1	846	548	2	5	1424	1364	10	9	616	638	16	2	388	390	17	5	301	244
23	1	470	499	3	5	944	985	12	9	324	338	17	2	789	806	18	5	964	1004
24	1	823	830	4	5	314	350	13	9	665	666	18	2	224	232	19	5	436	404
25	1	706	697	5	5	1629	1704	14	9	302	219	19	2	1108	1088	20	5	228	228
28	1	324	294	6	5	1256	1321	16	9	629	612	20	2	291	326	21	5	481	488
30	1	584	587	7	5	634	666	0	10	895	230	21	2	674	665	22	5	812	818
0	2	464	470	9	5	1051	1037	1	10	235	192	23	2	585	582	23	5	588	587
1	2	189	209	11	5	383	325	3	10	482	487	25	2	251	233	24	5	351	343
2	2	838	868	12	5	837	771	5	10	362	356	26	2	318	309	25	5	684	675
3	2	348	376	13	5	377	401	7	10	827	848	27	2	437	447	1	6	943	939
5	2	1145	1137	14	5	348	288	9	10	595	600	29	2	280	177	2	6	899	884
6	2	2736	2758	15	5	219	251	10	10	360	436	0	3	971	981	3	6	602	617
7	2	1670	1636	16	5	865	933	11	10	1471	1484	1	3	1069	1062	4	6	845	842
8	2	953	954	17	5	443	480	2	11	702	743	2	3	989	1008	5	6	1298	1302
9	2	203	136	19	5	236	235	3	11	288	314	3	3	723	683	7	6	308	319
10	2	257	148	20	5	843	825	4	11	325	318	5	3	1606	1590	8	6	275	288
11	2	1140	1135	21	5	839	881	6	11	781	731	6	3	972	980	9	6	929	911
12	2	777	751	23	5	340	321	**L = 1****				7	3	784	788	10	6	908	895
13	2	884	877	24	5	367	469	2	0	3852	4048	8	3	482	479	11	6	226	287
14	2	223	207	25	5	279	302	4	0	1482	1503	10	3	787	663	12	6	311	346
15	2	754	784	26	5	307	316	6	0	848	880	11	3	723	731	13	6	1219	1238
16	2	333	317	27	5	823	774	8	0	1284	1276	12	3	509	487	14	6	381	326
17	2	749	742	0	6	368	371	10	0	790	807	13	3	395	408	17	6	978	974
19	2	977	935	1	6	611	651	12	0	639	594	14	3	988	978	19	6	388	326
20	2	227	277	2	6	663	653	14	0	415	425	15	3	396	460	20	6	301	297
21	2	791	775	3	6	1043	1099	16	0	428	480	16	3	247	290	21	6	708	649
23	2	646	686	4	6	187	223	18	0	897	871	17	3	648	585	22	6	289	274
29	2	361	295	5	6	956	961	20	0	1663	1596	18	3	815	823	23	6	471	472
1	3	2957	3019	6	6	567	600	22	0	536	585	19	3	427	421	0	7	656	663
2	3	1812	1804	7	6	1317	1334	24	0	1303	1287	21	3	667	686	1	7	812	677
3	3	1488	1639	8	6	814	828	26	0	897	830	22	3	648	649	2	7	288	184
5	3	630	681	10	6	411	449	28	0	882	888	23	3	371	368	3	7	806	811
6	3	441	469	11	6	1246	1235	30	0	581	644	24	3	897	383	4	7	782	784
7	3	575	596	12	6	278	280	0	1	2186	2148	25	3	381	373	6	7	577	806
8	3	1287	1260	13	6	402	383	1	1	1388	1401	26	3	323	357	7	7	384	383
9	3	493	493	14	6	302	294	2	1	647	665	1	4	386	403	8	7	827	849
10	3	624	618	15	6	1642	1651	3	1	1023	982	2	4	1587	1489	10	7	988	986
11	3	875	141	16	6	370	377	4	1	617	630	3	4	762	744	11	7	383	317

Table 38 continued

H	K	FOBS	FCAL	H	K	FOBS	FCAL	H	K	FOBS	FCAL	H	K	FOBS	FCAL	H	K	FOBS	FCAL
**L =		10***		12	1	720	727	9	4	475	465	4	8	623	636	4	2	675	738
12	7	710	721	13	1	1838	1848	10	4	837	802	5	8	256	233	5	2	871	844
13	7	311	330	14	1	732	735	11	4	570	561	6	8	613	589	6	2	1053	1061
14	7	509	591	15	1	540	673	12	4	1091	1075	8	8	518	488	7	2	825	781
16	7	343	350	16	1	909	829	14	4	1249	1236	9	8	313	281	8	2	233	213
18	7	472	489	17	1	1041	1020	15	4	336	264	10	8	432	456	9	2	1432	1444
19	7	314	327	19	1	688	618	16	4	480	455	11	8	634	624	10	2	699	675
21	7	290	273	20	1	756	778	17	4	438	415	14	8	427	425	11	2	389	380
22	7	509	537	21	1	948	960	18	4	1008	1010	17	8	427	389	12	2	233	225
1	8	285	299	23	1	387	402	19	4	305	289	18	8	608	584	13	2	1382	1369
2	8	717	711	24	1	602	553	20	4	391	421	19	8	256	260	15	2	433	448
4	8	607	707	25	1	423	487	21	4	407	395	1	9	389	328	16	2	442	432
6	8	699	733	26	1	407	382	22	4	602	722	2	9	579	562	17	2	568	559
7	8	224	238	27	1	411	401	26	4	612	603	3	9	479	443	18	2	377	436
8	8	377	389	28	1	357	410	27	4	330	356	4	9	500	501	19	2	902	885
9	8	505	461	0	2	618	603	1	5	811	804	6	9	666	655	20	2	284	315
10	8	238	259	1	2	1087	1044	2	5	775	807	7	9	462	377	21	2	415	376
11	8	383	387	2	2	1948	1868	3	5	1609	1623	8	9	296	312	23	2	758	761
12	8	597	601	3	2	709	720	5	5	770	768	9	9	738	687	26	2	393	374
13	8	305	300	4	2	328	320	6	5	1329	1340	10	9	385	366	27	2	604	693
14	8	277	286	5	2	1488	1450	7	5	406	348	12	9	306	328	0	3	416	413
17	8	262	237	6	2	318	299	9	5	1340	1308	13	9	639	645	1	3	525	524
20	8	687	618	7	2	1318	1304	10	5	1230	1159	14	9	285	278	2	3	246	192
21	8	278	263	8	2	795	709	11	5	304	273	15	9	408	367	3	3	816	842
0	9	383	378	9	2	817	819	12	5	757	732	16	9	400	403	4	3	580	579
1	9	274	174	10	2	282	285	13	5	971	946	17	9	434	434	5	3	207	213
2	9	331	345	11	2	1687	1637	14	5	737	748	1	10	612	590	6	3	807	812
4	9	956	951	12	2	1044	1002	16	5	835	849	3	10	496	456	7	3	1080	1052
6	9	482	386	13	2	538	529	17	5	576	603	5	10	596	573	8	3	1137	1120
7	9	648	670	14	2	382	298	19	5	385	419	7	10	730	729	9	3	269	259
8	9	528	546	15	2	839	874	20	5	438	501	9	10	320	299	10	3	868	905
10	9	338	365	17	2	1184	1166	21	5	742	761	11	10	1183	1158	11	3	618	614
11	9	708	808	18	2	438	468	22	5	310	329	1	11	314	284	12	3	802	800
13	9	318	275	19	2	480	423	23	5	518	503	2	11	762	727	13	3	413	386
14	9	428	593	20	2	252	257	24	5	333	353	**L =		3***		14	3	676	887
16	9	488	471	21	2	939	959	25	5	251	215	2	0	2036	1985	15	3	802	826
17	9	530	514	23	2	387	247	0	6	972	946	4	0	801	800	17	3	317	330
1	10	328	313	24	2	378	403	1	6	1624	984	6	0	1066	1049	18	3	881	795
3	10	446	410	25	2	616	605	2	6	548	481	8	0	1415	1396	19	3	381	391
5	10	448	475	29	2	608	598	3	6	1385	1339	10	0	1690	1694	20	3	718	762
7	10	577	556	-1	3	885	841	4	6	500	587	12	0	1362	1365	21	3	461	439
9	10	1285	1216	2	3	1078	1077	5	6	515	522	14	0	1232	1262	23	3	389	388
10	10	258	258	3	3	998	885	6	6	266	207	16	0	613	613	24	3	493	534
11	10	246	188	4	3	775	786	7	6	1263	1263	18	0	574	616	25	3	509	441
13	10	1244	1216	5	3	630	637	8	6	788	740	20	0	1101	1098	1	4	265	242
0	11	577	580	6	3	848	848	9	6	355	314	24	0	900	887	2	4	260	268
2	11	313	246	7	3	170	191	11	6	772	788	26	0	383	389	3	4	376	401
4	11	789	796	8	3	339	311	12	6	473	483	28	0	523	470	4	4	378	373
5	11	388	348	9	3	913	896	14	6	217	178	0	1	383	394	5	4	741	715
**L =		2***		10	3	1100	1108	15	6	1062	1065	1	1	849	859	6	4	1309	1278
0	0	2899	2808	11	3	416	409	16	6	256	319	2	1	387	394	8	4	709	653
2	0	393	369	12	3	878	811	19	6	981	933	3	1	1015	987	9	4	829	808
4	0	664	663	13	3	477	491	20	6	431	426	4	1	1086	1136	10	4	1410	1442
6	0	1447	1461	14	3	215	248	21	6	295	290	5	1	1020	1024	11	4	287	251
8	0	1593	1609	15	3	462	447	22	6	258	235	6	1	932	900	12	4	957	986
10	0	1262	1265	16	3	996	983	23	6	559	535	7	1	660	649	14	4	752	703
12	0	2906	2906	17	3	804	757	1	7	617	640	8	1	926	907	15	4	285	302
14	0	684	684	18	3	559	514	2	7	727	748	9	1	441	449	16	4	1299	1278
16	0	980	935	19	3	719	730	3	7	465	423	10	1	649	632	18	4	241	213
18	0	1646	1632	20	3	777	727	5	7	792	753	11	1	1681	1692	19	4	488	484
20	0	478	488	21	3	447	512	6	7	841	838	12	1	845	831	20	4	766	743
22	0	1175	1254	22	3	435	427	7	7	392	430	15	1	1398	1419	24	4	418	395
26	0	683	627	23	3	421	468	8	7	408	416	17	1	431	442	0	5	1022	1088
28	0	372	366	26	3	280	291	9	7	411	383	18	1	478	457	1	5	989	950
1	1	1983	1941	27	3	431	425	10	7	771	757	19	1	820	817	3	5	917	896
2	1	1615	1580	28	3	339	289	11	7	413	413	22	1	642	662	4	5	672	648
3	1	829	851	0	4	787	782	12	7	987	988	23	1	346	386	5	5	428	421
4	1	1408	1329	1	4	199	191	14	7	597	576	24	1	268	260	6	5	296	382
5	1	1999	1932	2	4	875	845	16	7	637	638	25	1	374	378	7	5	936	933
6	1	743	699	3	4	747	715	20	7	591	592	26	1	471	430	8	5	988	1001
7	1	782	715	4	4	1218	1180	21	7	401	328	27	1	257	296	10	5	658	641
8	1	1083	1078	5	4	422	427	0	8	748	740	28	1	368	341	11	5	854	877
9	1	962	949	6	4	769	797	1	8	261	282	1	2	896	867	12	5	989	978
10	1	995	996	7	4	370	329	2	8	291	295	2	2	476	484	14	5	644	620
11	1	196	233	8	4	983	973	3	8	471	472	3	2	668	648	18	5	731	758

Table 38 continued

H	K	FOBS	FCAL
**L =		3*****	
16	5	702	655
17	5	310	320
18	5	458	416
19	5	837	851
21	5	327	395
23	5	650	630
25	5	315	246
1	6	1388	1393
2	6	568	554
3	6	877	883
4	6	474	494
5	6	1297	1312
6	6	329	371
7	6	450	478
8	6	248	269
9	6	919	907
10	6	415	354
12	6	264	280
13	6	748	742
14	6	310	311
16	6	340	317
17	6	989	1004
18	6	384	332
19	6	326	356
21	6	396	449
23	6	608	606
0	7	861	847
3	7	696	678
4	7	792	740
5	7	439	435
6	7	375	398
7	7	656	641
8	7	942	970
9	7	586	587
10	7	238	222
12	7	503	457
13	7	274	284
14	7	478	458
18	7	680	647
19	7	528	517
1	8	375	422
2	8	630	636
4	8	482	463
5	8	387	381
6	8	330	319
7	8	872	860
8	8	843	819
9	8	350	314
12	8	599	623
13	8	516	541
15	8	604	545
16	8	601	606
19	8	354	376
0	9	537	558
1	9	586	600
4	9	654	713
5	9	485	467
7	9	374	345
8	9	609	641
11	9	611	564
12	9	289	292
13	9	364	330
14	9	357	385
16	9	618	610
1	10	736	724
2	10	344	302
3	10	634	624
5	10	676	711
7	10	346	354
9	10	863	866
**L =		4*****	
0	0	1486	1434
2	0	776	811
4	0	1803	1793
6	0	1525	1515
8	0	1477	1445
10	0	1294	1198
12	0	1721	1694
14	0	600	589
16	0	415	437
18	0	948	978
20	0	734	693
22	0	1111	1150
24	0	529	548
1	1	1178	1137
2	1	1152	1100
3	1	748	768
4	1	410	431
5	1	1739	1718
6	1	767	772
7	1	404	378
8	1	524	572
9	1	1055	1016
10	1	508	548
11	1	244	248
12	1	516	494
13	1	1092	1086
14	1	329	371
15	1	235	227
16	1	311	231
17	1	784	784
20	1	387	363
21	1	657	657
22	1	410	425
24	1	624	655
25	1	360	375
26	1	474	438
27	1	458	407
0	2	349	355
1	2	916	865
2	2	518	552
3	2	1154	1098
4	2	627	644
5	2	515	471
6	2	932	911
7	2	618	624
8	2	644	624
11	2	1033	1072
12	2	545	548
13	2	559	573
14	2	268	250
15	2	781	788
16	2	237	232
17	2	484	488
18	2	440	398
19	2	294	338
21	2	518	529
24	2	321	286
25	2	780	815
27	2	242	161
1	3	184	166
3	3	297	231
4	3	354	303
5	3	1012	1006
6	3	764	766
7	3	296	288
8	3	280	328
9	3	1044	1006
10	3	932	915
11	3	273	313
12	3	934	937
13	3	965	962
14	3	223	223
15	3	957	970
16	3	590	587
18	3	391	422
19	3	378	381
20	3	577	606
21	3	393	388
22	3	468	456
23	3	389	377
24	3	248	152
26	3	254	251
0	4	715	754
2	4	271	273
3	4	405	347
4	4	1173	1170
5	4	486	443
6	4	631	644
7	4	334	380
8	4	1233	1242
9	4	813	764
10	4	835	870
11	4	275	269
12	4	.31	757
14	4	1061	1051
15	4	424	360
16	4	385	409
17	4	388	382
18	4	776	790
20	4	296	222
22	4	490	490
25	4	290	307
1	5	1341	1330
2	5	671	770
3	5	563	530
4	5	584	508
5	5	962	992
6	5	766	760
7	5	570	553
8	5	297	311
9	5	562	571
10	5	1030	1066
12	5	577	616
13	5	538	564
14	5	589	564
15	5	394	316
16	5	598	600
17	5	561	548
18	5	345	292
19	5	368	314
20	5	275	291
21	5	603	605
23	5	300	331
24	5	387	425
0	6	624	686
1	6	1092	1144
2	6	482	456
3	6	1084	1107
4	6	486	476
5	6	401	377
6	6	364	404
7	6	1218	1178
11	6	700	681
14	6	898	381
15	6	589	629
16	6	313	335
19	6	723	768
20	6	318	287
21	6	807	816
22	6	274	293
1	7	817	803
2	7	984	932
5	7	600	604
6	7	822	821
7	7	420	394
8	7	451	489
9	7	385	388
10	7	463	495
11	7	374	374
12	7	425	488
13	7	703	679
17	7	449	467
20	7	625	629
0	8	517	532
2	8	312	301
3	8	246	140
4	8	335	356
5	8	268	317
6	8	383	417
8	8	423	449
10	8	474	461
11	8	324	227
12	8	422	391
13	8	437	392
14	8	775	778
17	8	264	326
1	9	393	381
2	9	726	732
3	9	426	464
4	9	270	242
5	9	384	329
6	9	628	672
8	9	265	244
9	9	488	348
10	9	380	383
12	9	291	268
13	9	397	398
1	10	737	689
3	10	595	635
5	10	651	761
7	10	612	649
**L =		5*****	
2	0	1180	1201
4	0	1786	1687
6	0	1161	1146
8	0	1560	1529
10	0	1335	1293
12	0	631	626
14	0	693	714
16	0	464	416
18	0	764	702
20	0	878	861
22	0	473	500
24	0	847	788
26	0	292	357
0	1	822	825
1	1	384	333
2	1	548	543
3	1	1599	1574
4	1	725	732
5	1	205	174
6	1	840	815
7	1	1330	1334
8	1	677	677
9	1	370	334
10	1	651	680
11	1	813	793
12	1	283	265
13	1	202	197
14	1	286	276
15	1	680	666
16	1	263	240
19	1	693	689
21	1	280	263
22	1	521	494
23	1	506	583
24	1	829	825
25	1	581	536
26	1	780	721
1	2	906	911
2	2	489	372
3	2	882	865
5	2	984	987
6	2	497	500
7	2	407	387
8	2	263	230
9	2	904	901
11	2	394	397
12	2	209	193
13	2	767	749
14	2	229	245
15	2	311	227
16	2	361	346
17	2	411	447
23	2	723	699
0	3	419	471
1	3	246	173
2	3	282	270
3	3	470	489
4	3	348	349
5	3	519	509
6	3	410	425
7	3	1101	1082
8	3	466	448
9	3	289	286
10	3	648	617
11	3	918	933
14	3	646	667
15	3	689	608
17	3	278	178
18	3	605	622
19	3	262	223
20	3	421	431
21	3	247	252
22	3	291	274
1	4	699	686
2	4	987	974
3	4	218	213
4	4	477	448
6	4	1069	1103
7	4	473	503
8	4	964	968
9	4	369	341
10	4	847	858
11	4	449	452
12	4	889	898
13	4	646	640
14	4	601	600
15	4	293	271
16	4	782	786
19	4	288	271
20	4	470	484
21	4	265	325
0	5	638	648
1	5	870	896
3	5	947	969
4	5	581	580
5	5	240	252
6	5	452	391
7	5	703	691
8	5	1186	1143
9	5	414	441
10	5	768	722
11	5	366	392
12	5	998	991
14	5	608	572
15	5	520	507
16	5	298	270
17	5	261	287
18	5	480	416
19	5	659	655
22	5	324	318
1	6	918	907
2	6	882	908
3	6	538	574
4	6	358	380
5	6	1084	1057
6	6	827	818
10	6	880	886
13	6	514	500
14	6	241	193
17	6	723	699
18	6	410	426

Table 38 continued

H	K	FOBS	FCAL	H	K	FOBS	FCAL	H	K	FOBS	FCAL	H	K	FOBS	FCAL	H	K	FOBS	FCAL
L = 5**				23	2	345	289	***L = 7*****				0	5	594	598	5	3	265	288
19	6	316	300	1	3	487	445	2	0	1356	1417	1	5	453	496	7	3	404	395
2C	6	313	246	2	3	664	668	4	0	709	715	3	5	685	655	10	3	376	353
0	7	1306	1341	3	3	488	481	6	0	1034	1053	4	5	634	641	12	3	532	603
3	7	478	491	4	3	583	518	8	0	318	300	7	5	721	758	13	3	512	542
4	7	909	901	5	3	540	555	10	C	763	705	8	5	609	612	15	3	397	418
5	7	251	243	6	3	462	430	12	0	411	373	10	5	421	446	16	3	647	720
7	7	324	354	8	3	350	349	14	0	476	477	11	5	539	570	0	4	725	722
8	7	348	395	9	3	517	523	16	0	607	676	12	5	587	549	1	4	340	344
9	7	370	328	10	3	222	282	18	0	685	717	14	5	427	437	4	4	774	780
10	7	380	392	12	3	478	575	20	C	934	982	15	5	558	486	5	4	275	347
14	7	619	581	13	3	630	618	0	1	756	758	17	5	327	308	8	4	648	649
19	7	642	630	16	3	676	659	1	1	453	516	1	6	590	583	10	4	415	408
2	8	582	586	17	3	330	338	2	1	376	405	2	6	450	411	12	4	394	385
4	8	386	381	18	3	392	418	3	1	699	699	3	6	433	462	14	4	476	519
6	8	321	367	19	3	267	174	4	1	546	564	4	6	416	361	1	5	462	494
7	8	289	316	22	3	370	369	5	1	532	539	5	6	878	923	2	5	644	642
8	8	344	325	0	4	885	836	6	1	435	422	6	6	381	317	3	5	481	480
10	8	381	350	3	4	294	243	7	1	891	895	8	6	325	368	4	5	520	482
11	8	283	231	4	4	955	975	8	1	306	305	9	6	741	723	7	5	384	402
12	8	650	648	5	4	303	327	9	1	346	412	10	6	352	352	9	5	672	688
15	8	402	371	6	4	508	508	10	1	314	335	13	6	811	630	10	5	404	378
0	9	972	941	7	4	267	312	11	1	681	620	14	6	264	261	12	5	260	299
1	9	394	403	8	4	953	955	12	1	324	262	0	7	437	503	0	6	287	281
3	9	289	317	10	4	446	472	14	1	364	361	1	7	306	387	1	6	301	360
4	9	642	606	11	4	693	682	15	1	725	750	3	7	406	442	2	6	249	303
8	9	433	420	12	4	619	625	16	1	428	409	4	7	481	500	3	6	638	649
L = 6**				14	4	821	799	18	1	636	640	5	7	365	369	7	6	740	731
0	0	2035	2008	15	4	306	284	19	1	598	610	6	7	395	378	8	6	372	384
2	0	563	596	18	4	674	709	21	1	415	370	7	7	305	333	***L = 9*****			
4	0	1578	1651	19	4	298	308	1	2	276	309	8	7	403	370	2	0	1621	1564
6	0	1067	1077	1	5	706	746	3	2	290	300	9	7	258	249	4	0	453	393
8	0	561	569	2	5	646	646	4	2	554	575	10	7	405	388	6	C	722	699
10	0	783	788	3	5	263	254	5	2	954	928	2	8	659	702	8	0	496	521
12	0	642	680	5	5	1C78	1097	7	2	466	471	***L = 8*****				10	C	571	534
14	0	585	548	6	5	860	800	9	2	982	911	0	0	1447	1466	12	0	411	448
16	0	768	830	8	5	902	491	10	2	338	324	2	0	297	330	C	1	479	490
18	0	482	481	9	5	667	670	12	2	338	288	4	0	1214	1194	1	1	663	682
20	0	646	680	10	5	940	930	13	2	892	934	8	0	736	759	2	1	326	332
22	0	945	986	12	5	647	637	14	2	363	373	12	0	552	573	3	1	491	474
24	0	362	319	13	5	390	293	15	2	671	983	14	0	527	540	4	1	483	447
1	1	817	781	14	5	659	667	16	2	550	476	16	0	336	325	5	1	604	610
2	1	812	796	16	5	481	448	17	2	648	717	18	0	591	572	6	1	467	420
3	1	462	432	17	5	605	607	19	2	628	579	1	1	379	405	7	1	907	922
4	1	784	786	20	5	414	397	21	2	450	485	2	1	531	526	8	1	317	321
5	1	1004	1189	0	6	871	890	0	3	433	378	3	1	706	688	9	1	406	388
6	1	611	633	1	6	649	622	1	3	422	426	4	1	470	467	11	1	583	565
7	1	347	321	3	6	980	953	3	3	648	678	5	1	586	583	12	1	326	291
8	1	789	782	4	6	430	426	4	3	330	368	7	1	719	738	3	2	339	339
9	1	823	847	5	6	375	357	5	3	496	511	8	1	297	350	4	2	328	316
10	1	439	379	6	6	361	358	6	3	495	459	9	1	677	669	5	2	626	587
12	1	320	330	7	6	963	958	7	3	389	373	12	1	418	384	6	2	384	376
13	1	777	747	8	6	270	223	8	3	447	438	13	1	679	692	7	2	291	291
14	1	392	396	11	6	653	675	10	3	232	188	14	1	252	171	9	2	544	524
17	1	728	728	12	6	276	188	11	3	626	652	15	1	252	263	1C	2	293	290
2C	1	392	430	15	6	628	608	13	3	336	392	16	1	600	606	1	3	660	650
21	1	498	482	16	6	426	444	14	3	943	926	17	1	660	661	3	3	456	498
22	1	889	905	1	7	362	341	15	3	519	543	1	2	290	225	4	3	316	283
23	1	483	423	2	7	981	923	17	3	481	359	2	2	416	415	5	3	338	403
24	1	827	838	4	7	381	350	18	3	442	486	3	2	242	319	8	3	354	368
1	2	449	486	5	7	460	418	19	3	425	423	5	2	448	417	1C	3	303	284
3	2	968	980	6	7	728	719	20	3	488	378	6	2	385	320	11	3	301	295
4	2	448	469	7	7	262	274	2	4	862	880	7	2	429	419	2	4	659	672
6	2	287	215	9	7	277	294	6	4	725	773	8	2	363	389	5	4	286	290
7	2	982	961	12	7	368	353	7	4	376	398	11	2	743	749	6	4	743	745
8	2	361	312	13	7	291	293	8	4	260	298	12	2	389	328	1	5	318	281
11	2	928	941	15	7	323	314	9	4	295	304	13	2	872	885	***L = 10*****			
14	2	327	349	0	8	862	878	10	4	598	571	14	2	389	394	0	C	813	853
15	2	694	689	4	8	634	598	12	4	599	527	15	2	895	914	4	0	862	838
18	2	318	248	5	8	384	316	13	4	218	253	17	2	776	809	1	1	521	514
19	2	364	369	9	8	287	269	14	4	521	499	1	3	448	378	2	1	519	494
2C	2	276	286	10	8	474	490	15	4	298	225	3	3	687	642	3	1	348	328
21	2	671	670	2	9	388	367	16	4	711	718	4	3	286	295				

Table 39

Atomic Coordinates and Isotropic Temperature Factors

Name	x	y	z	B*
Rh	0.11298(3)	0.12204(7)	-0.25000	2.25
Cℓ	0.0770(1)	0.0895(3)	-0.4336(4)	5.07
P1	0.12326(9)	-0.0662(2)	-0.2471(6)	2.28
P2	0.1655(1)	0.1689(3)	-0.1363(4)	2.39
P3	0.0729(1)	0.2767(3)	-0.2305(5)	2.61

* These values are equivalent isotropic temperature factors corresponding to the anisotropic temperature factors given in Table 40

(Table continued)

Table 39 continued

(a) Phenyl Carbon Rigid Bodies

Name	x	y	z	B
C111	0.0719(2)	-0.1234(8)	-0.2267(7)	2.4(3)
C112	0.0441(3)	-0.0622(6)	-0.1603(9)	4.3(4)
C113	0.0055(3)	-0.1035(7)	-0.1377(8)	4.5(4)
C114	-0.0053(2)	-0.2059(8)	-0.1815(7)	4.6(4)
C115	0.0225(3)	-0.2671(6)	-0.2478(9)	4.7(3)
C116	0.0611(3)	-0.2258(7)	-0.2704(8)	3.1(3)
D	0.431(6)	$x^{1\frac{1}{2}}$	0.0333(2)	
E	0.374(7)	$y^{1\frac{1}{2}}$	-0.1646(5)	
F	0.412(6)	$z^{1\frac{1}{2}}$	-0.2041(6)	
C121	0.1444(3)	-0.1377(9)	-0.3768(7)	2.0(4)
C122	0.1535(3)	-0.2484(8)	-0.3710(8)	3.2(4)
C123	0.1722(3)	-0.2995(6)	-0.469(1)	5.6(5)
C124	0.1819(3)	-0.2400(9)	-0.5726(7)	4.6(5)
C125	0.1728(3)	-0.1293(8)	-0.5784(8)	4.4(4)
C126	0.1540(3)	-0.0782(6)	-0.481(1)	3.7(4)
D	6.065(6)	x^{1}	0.1631(2)	
E	1.162(6)	y^{1}	-0.1888(6)	
F	2.662(7)	z^{1}	-0.4747(6)	
C131	0.1510(5)	-0.1328(7)	-0.121(2)	2.1(4)
C132	0.1303(6)	-0.1529(7)	-0.0126(9)	3.0(4)
C133	0.1503(8)	-0.2012(7)	0.085(2)	4.0(4)
C134	0.1911(5)	-0.2294(7)	0.074(2)	4.0(4)

(Table continued)

Name	x	y	z	B
C135	0.2118(6)	-0.2093(7)	-0.0335(9)	3.0(3)
C136	0.1918(8)	-0.1611(7)	-0.131(2)	2.9(3)
D	5.154(5)	x^1	0.1710(2)	
E	0.66(1)	y^1	-0.1811(4)	
F	1.47(1)	z^1	-0.0231(6)	
C211	0.2107(3)	0.0905(6)	-0.183(3)	2.7(4)
C212	0.2409(8)	0.0560(9)	-0.104(1)	4.3(4)
C213	0.2751(6)	0.0026(8)	-0.149(2)	3.6(4)
C214	0.2790(3)	-0.0163(6)	-0.273(3)	3.5(4)
C215	0.2488(8)	0.0182(9)	-0.352(1)	6.1(5)
C216	0.2146(6)	0.0716(8)	-0.308(2)	4.3(5)
D	5.210(5)	x^1	0.2448(2)	
E	1.79(2)	y^1	0.0371(4)	
F	1.74(2)	z^1	-0.2281(8)	
C221	0.1842(3)	0.3102(6)	-0.164(1)	1.6(3)
C222	0.1737(3)	0.3948(9)	-0.0855(7)	3.1(3)
C223	0.1869(3)	0.5004(7)	-0.1094(9)	4.1(4)
C224	0.2106(3)	0.5214(6)	-0.212(1)	4.2(4)
C225	0.2211(3)	0.4368(9)	-0.2896(7)	5.5(5)
C226	0.2079(3)	0.3312(7)	-0.2657(9)	4.7(4)
D	3.311(6)	x^1	0.1974(2)	
E	0.996(5)	y^1	0.4158(5)	
F	1.906(6)	z^1	-0.1875(6)	

(Table continued)

Name	x	y	z	B
C231	0.1657(8)	0.1601(9)	0.0305(7)	2.9(3)
C232	0.1326(5)	0.1091(8)	0.084(2)	3.8(4)
C233	0.1292(4)	0.1059(7)	0.210(2)	5.7(5)
C234	0.1591(8)	0.1536(9)	0.2825(7)	6.9(5)
C235	0.1922(5)	0.2045(8)	0.229(2)	5.6(4)
C236	0.1955(4)	0.2078(7)	0.103(2)	4.2(4)
D	4.186(5)	x^1	0.1624(2)	
E	1.54(1)	y^1	0.1568(5)	
F	6.22(1)	z^1	0.1565(7)	
C311	0.0767(3)	0.3751(9)	-0.105(1)	2.8(4)
C312	0.0794(3)	0.3329(6)	0.012(1)	3.4(4)
C313	0.0834(3)	0.403(1)	0.1107(9)	5.4(4)
C314	0.0846(3)	0.5151(9)	0.092(1)	6.9(6)
C315	0.0819(3)	0.5573(6)	-0.025(1)	7.9(6)
C316	0.0779(3)	0.487(1)	-0.1235(9)	4.8(4)
D	3.183(6)	x^1	0.0806(2)	
E	1.658(7)	y^1	0.4451(6)	
F	0.665(8)	z^1	-0.0064(8)	
C321	0.0700(5)	0.3672(8)	-0.361(1)	3.4(4)
C322	0.0363(3)	0.432(1)	-0.384(1)	5.7(5)
C323	0.0366(3)	0.5048(8)	-0.4815(9)	6.0(5)
C324	0.0707(5)	0.5120(8)	-0.556(1)	5.0(5)
C325	0.1044(3)	0.447(1)	-0.533(1)	7.0(5)

(Table continued)

Name	x	y	z	B
C326	0.1040(3)	0.3743(8)	-0.4358(9)	4.6(4)
D	2.351(6)	x^1	0.0703(2)	
E	0.567(9)	y^1	0.4396(6)	
F	2.00(1)	z^1	-0.4586(7)	
C331	0.0202(3)	0.2307(7)	-0.212(4)	3.3(4)
C332	0.003(1)	0.2158(9)	-0.098(3)	4.4(4)
C333	-0.037(1)	0.175(1)	-0.089(1)	6.4(5)
C334	-0.0585(3)	0.1501(7)	-0.193(4)	5.9(5)
C335	-0.041(1)	0.1650(9)	-0.307(3)	11.3(8)
C336	-0.002(1)	0.205(1)	-0.316(1)	7.3(6)
D	1.203(5)	x^1	-0.0191(2)	
E	1.49(2)	y^1	0.1904(4)	
F	1.42(2)	z^1	-0.2027(7)	

ǂ These values represent the ring centre of gravity coordinates

(Table continued)

(b) Phenyl Hydrogen Rigid Bodies

Name	x	y	z	B
H112	0.051	0.011	-0.129	4.7
H113	-0.014	-0.060	-0.090	5.0
H114	-0.033	-0.236	-0.165	5.1
H115	0.015	-0.341	-0.279	5.2
H116	0.081	-0.270	-0.318	3.4
D	0.431			
E	0.374			
F	1.459			
H122	0.147	-0.291	-0.296	3.5
H123	0.179	-0.379	-0.464	6.1
H124	0.196	-0.277	-0.643	5.1
H125	0.180	-0.087	-0.653	5.9
H126	0.147	0.001	-0.485	4.1
D	6.065			
E	1.162			
F	3.709			
H132	0.101	-0.132	-0.005	3.3
H133	0.135	-0.215	0.162	4.4
H134	0.205	-0.264	0.144	4.4
H135	0.241	-0.230	-0.041	3.3
H136	0.207	-0.147	-0.208	3.2

(Table continued)

Name	x	y	z	B
D	5.154			
E	0.66			
F	2.51			
H212	0.238	0.070	-0.014	4.7
H213	0.297	-0.022	-0.091	4.0
H214	0.303	-0.055	-0.305	3.8
H215	0.252	0.005	-0.441	6.7
H216	0.193	0.097	-0.365	4.7
D	5.210			
E	1.79			
F	2.78			
H222	0.157	0.380	-0.012	3.4
H223	0.179	0.561	-0.053	4.5
H224	0.220	0.597	-0.229	4.6
H225	0.238	0.452	-0.363	6.1
H226	0.216	0.270	-0.322	5.2
D	3.311			
E	0.996			
F	2.953			
H232	0.111	0.075	0.033	4.2
H233	0.106	0.069	0.249	6.3
H234	0.157	0.151	0.373	7.6
H235	0.214	0.239	0.280	6.2

(Table continued)

Name	x	y	z	B
H236	0.219	0.245	0.064	4.6
D	4.186			
E	1.54			
F	0.99			
H312	0.079	0.252	0.025	3.7
H313	0.085	0.372	0.195	5.9
H314	0.087	0.565	0.164	7.6
H315	0.082	0.638	-0.037	8.7
H316	0.076	0.518	-0.207	5.3
D	3.183			
E	1.658			
F	1.712			
H322	0.012	0.427	-0.330	6.3
H323	0.012	0.552	-0.498	6.6
H324	0.071	0.564	-0.626	5.5
H325	0.129	0.452	-0.587	7.7
H326	0.128	0.327	-0.420	5.1
D	2.351			
E	0.567			
F	3.047			
H332	0.018	0.234	-0.023	4.9
H333	-0.049	0.165	-0.007	7.1
H334	-0.087	0.121	-0.186	6.5

(Table continued)

Name	x	y	z	B
H335	-0.057	0.147	-0.382	12.4
H336	0.011	0.216	-0.398	8.1
D	1.203			
E	1.49			
F	2.46			

Table 40

Anisotropic Temperature Factors ($\mathring{A}^2 \times 10^3$)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Rh	29.6(5)	25.0(5)	31.0(6)	1.1(6)	- 5(1)	- 3(1)
Cl	75(3)	53(3)	64(3)	13(2)	-43(3)	-13(3)
P1	28(2)	28(2)	30(2)	0(1)	- 1(3)	- 5(5)
P2	32(2)	27(2)	32(3)	2(2)	0(2)	- 2(2)
P3	35(2)	32(2)	32(3)	2(2)	3(3)	1(3)

Table 41

Selected Interatomic Distances

Atom 1	Atom 2	Distance (Å)	
Rh	Cl	2.376(4)	2.398(4)*
Rh	P1	2.334(3)	2.334(3)*
Rh	P2	2.214(4)	2.214(4)*
Rh	P3	2.322(4)	2.324(4)*
P1	C111	1.842(6)	
P1	C121	1.815(9)	
P1	C131	1.859(8)	
P2	C211	1.847(7)	
P2	C221	1.864(7)	
P2	C231	1.839(9)	
P3	C311	1.837(9)	
P3	C321	1.820(9)	
P3	C331	1.838(8)	

* Value corrected for riding

Table 42

Selected Intramolecular Angles

Atom 1	Atom 2	Atom 3	Angle (°)
P1	Rh	P2	97.9(2)
P1	Rh	P3	152.8(1)
P1	Rh	Cℓ	85.2(2)
P1	Rh	H112	67.2
P2	Rh	P3	100.4(1)
P2	Rh	Cℓ	156.2(2)
P2	Rh	H112	115.1
P3	Rh	Cℓ	86.1(2)
P3	Rh	H112	86.7
Cℓ	Rh	H112	88.0
P1	C111	C114	176.6(7)
P1	C121	C124	176.0(6)
P1	C131	C134	178.2(6)
P2	C211	C214	174.9(7)
P2	C221	C224	178.1(6)
P2	C231	C234	175.0(7)
P3	C311	C314	176.7(8)
P3	C321	C324	176.0(7)
P3	C331	C334	176.4(7)
Rh	P1	C111	104.3(3)
Rh	P1	C121	121.5(4)
Rh	P1	C131	121.1(4)

(Table continued)

Atom 1	Atom 2	Atom 3	Angle (°)
Rh	P2	C211	109.7(4)
Rh	P2	C221	114.1(3)
Rh	P2	C231	123.5(4)
Rh	P3	C311	124.7(4)
Rh	P3	C321	117.1(4)
Rh	P3	C331	107.2(3)
C111	P1	C121	105.3(5)
C111	P1	C131	101.2(5)
C121	P1	C131	100.8(4)
C211	P2	C221	100.0(4)
C211	P2	C231	104.3(6)
C221	P2	C231	102.4(5)
C311	P3	C321	101.3(5)
C311	P3	C331	100.4(5)
C321	P3	C331	103.0(5)

Table 43

Selected Intramolecular Non-bonded Contacts

Atom 1	Atom 2	Distance (Å)
Rh	H112	2.77
Rh	H216	2.94
Cℓ	H126	2.62
Cℓ	H336	2.70
H116	H122	2.18
H126	H216	2.31
H212	H236	2.39
H216	H226	2.31
H312	H332	2.07
C111	H132	2.62
C112	H132	2.68
C122	H116	2.47
C211	H226	2.69
C216	H226	2.44
C231	H212	2.68
C232	H312	2.59
C236	H212	2.55
C312	H332	2.38
C312	H222	2.62
C321	H316	2.51
C322	H316	2.56
C111	C121	2.91(1)

(Table continued)

Atom 1	Atom 2	Distance (Å)
C111	C131	2.86(1)
C121	C131	2.83(1)
C211	C221	2.84(1)
C211	C231	2.91(1)
C221	C231	2.83(1)
C311	C321	2.82(1)
C311	C331	2.82(1)
C321	C331	2.86(1)
C126	C216	3.32(1)
C131	C211	3.44(1)
C132	C232	3.38(1)
C135	C212	3.48(1)
C136	C211	3.20(1)
C136	C212	3.13(1)
C136	C213	3.40(1)
C222	C312	3.37(1)
C222	C316	3.36(1)
P1	P2	3.430(5)
P2	P3	3.485(5)
P1	Cℓ	3.208(6)
P3	Cℓ	3.190(6)

Table 44

Selected Intermolecular Contacts

Atom 1	Atom 2	Symmetry Operation (on atom 2)	Distance (Å)
Cℓ	H113	$\bar{x}$, $\bar{y}$, 1/2+z-1	2.71
H123	H213	1/2-x, 1/2+y-1, 1/2+z-1	2.38
H124	H134	x, y, z-1	2.37
H126	H234	x, y, z-1	2.43
H132	H335	$\bar{x}$, $\bar{y}$, 1/2+z	2.00
H212	H225	1/2-x, 1/2+y-1, 1/2+z	2.34
H213	H325	1/2-x, 1/2+y-1, 1/2+z	2.47

Fig. 14

A General View of the Red Form of $RhCl(P(C_6H_5)_3)_3$

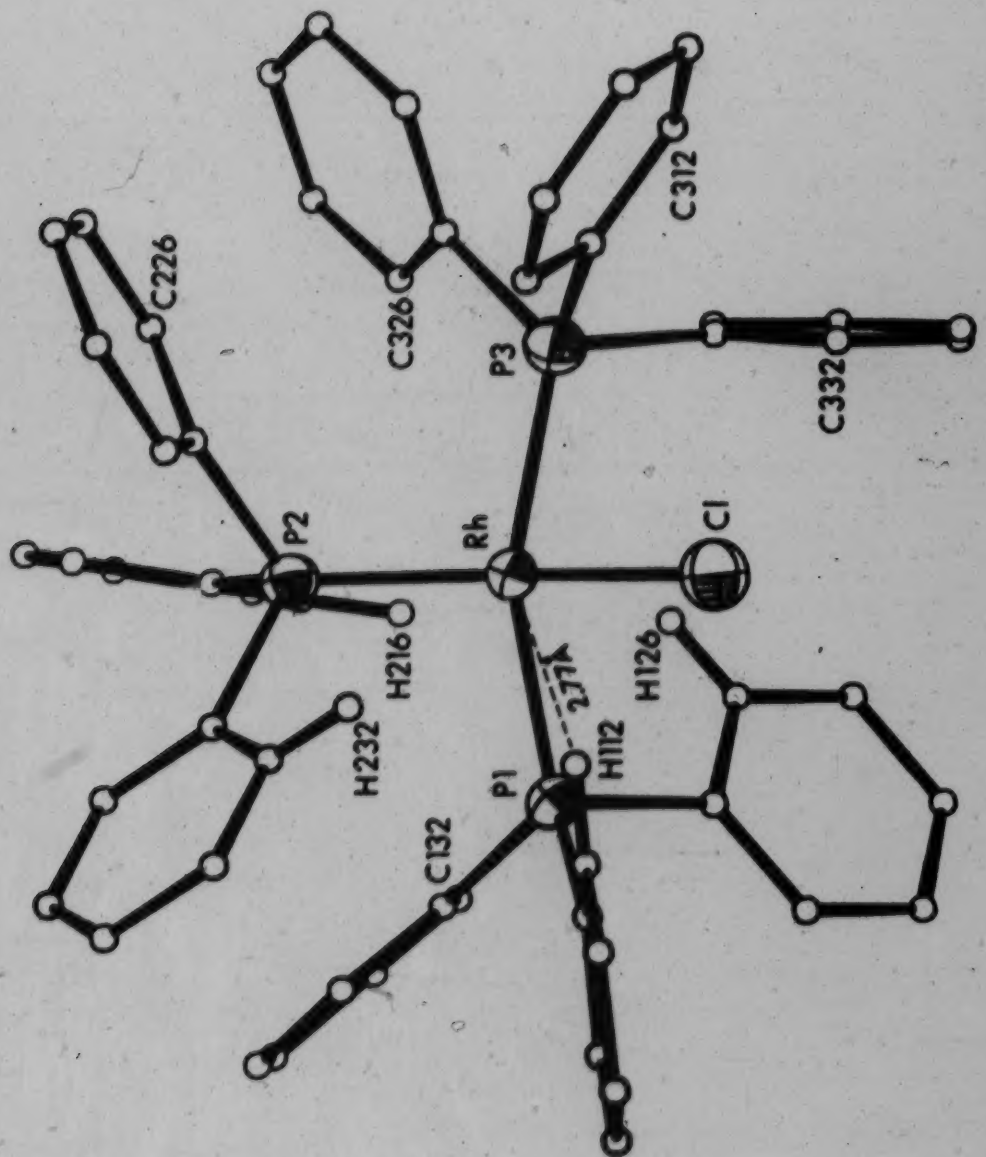


Fig. 15

Central Geometry Viewed down the P1-P3 Direction

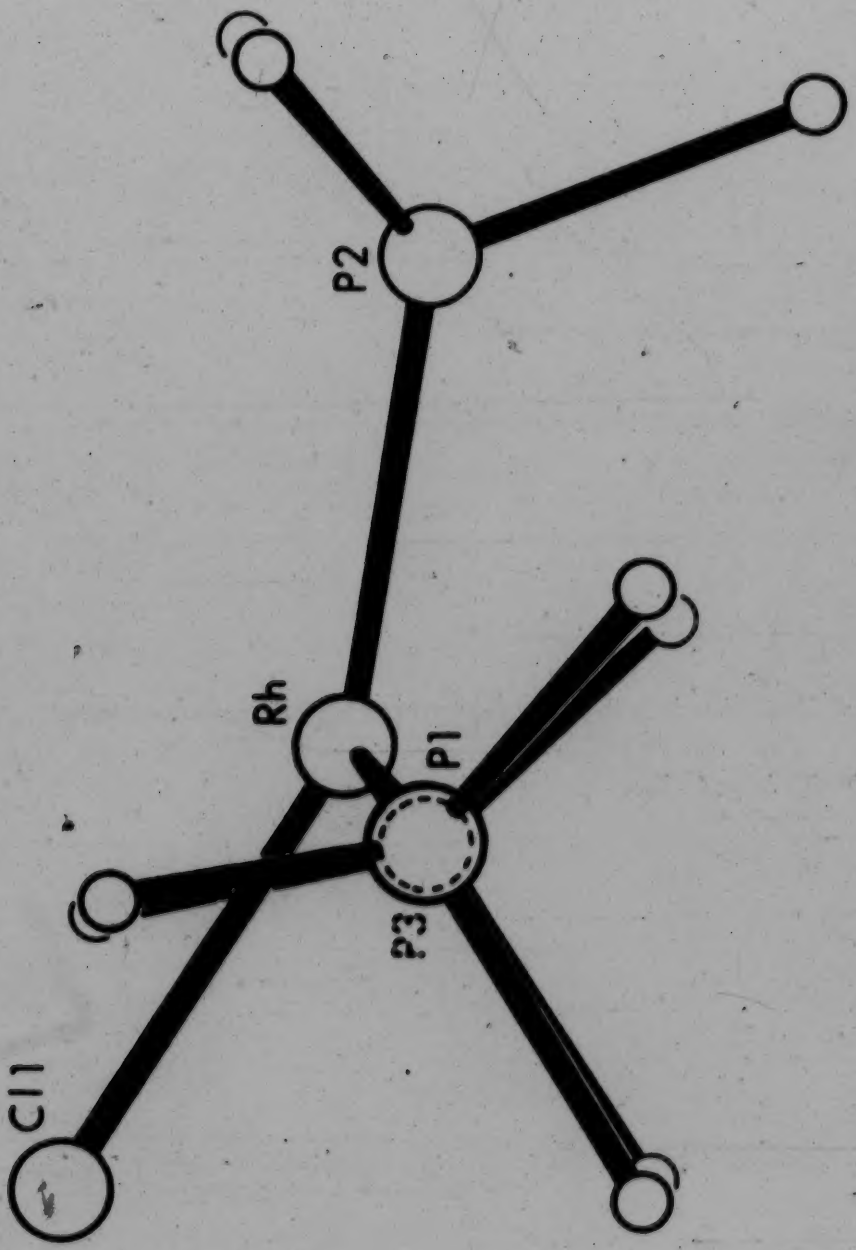
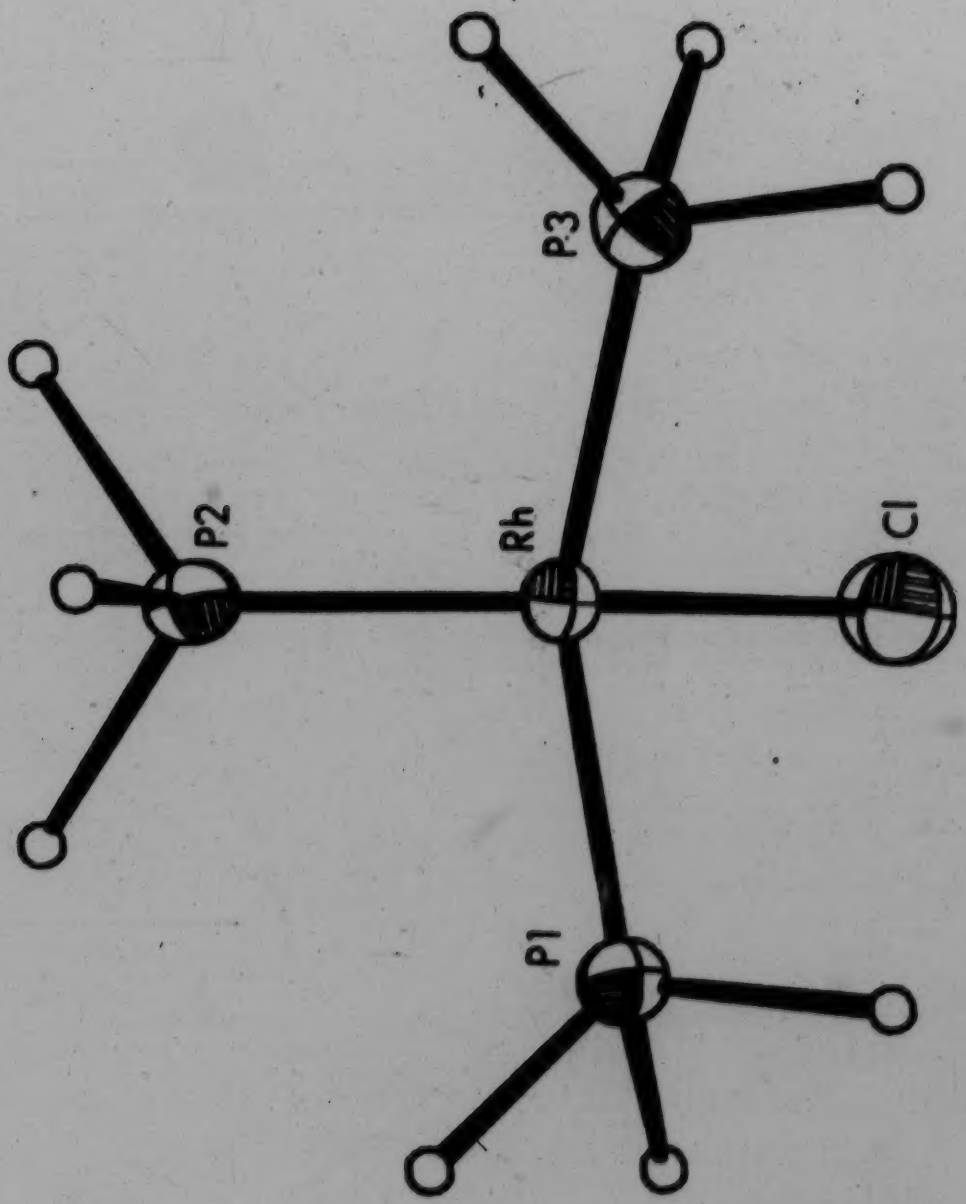


Fig. 16

View Perpendicular to the P1-P2-P3 Plane



Discussion

The molecular structure of $RhCl(P(C_6H_5)_3)_3$ in the red crystalline modification is shown in Fig. 14. Simplified views of the central portion of the molecule are given in Figs. 15 and 16. These diagrams should be compared with Figs. 11, 12 and 13 to observe the major differences and similarities between the molecular structure in the red and orange allotropes. To a first approximation the rhodium coordination is square planar but a pronounced distortion towards a tetrahedral geometry is evident in Fig. 15. This distortion is greater than that observed for the orange modification as is clearly indicated by a comparison of Cl-Rh-P2 angles - 156.2(2)° (red) and 166.7(2)° (orange) - and P1-Rh-P3 angles - 152.8(1)° (red) and 159.1(2)° (orange). The actual deviations from planarity for the $RhClP_3$ fragment are given in Table 45. The magnitude of the distortion in the red form is sufficiently great that the only significant interligand repulsions occur between ligands directly bonded to rhodium. Both forms distort from the planar geometry in the same way i.e. towards a tetrahedral geometry. This should be compared with a pyramidal distortion observed in RhLCl (where L is the tridentate phosphine ligand $(C_6H_5)P((C_3H_6)P(C_6H_5)_2)_2$ [140].

Table 45

Weighted Mean Molecular Planes for $RhCl(P(C_6H_5)_3)_3$ [a]

Atoms Contained in the Planes	Modification	Equation
Rh, Cl, P1, P2, P3	red	-0.6629X - 0.2857Y + 0.2690Z = -4.8112
.. ..	orange	-0.1624X + 0.1708Y + 0.9718Z = 4.2984

Distances of Atoms from Planes

Atom	Distance (Å)	
	red	orange
Rh	0.010	-0.014
Cl	-0.489	-0.290
P1	0.469	0.419
P2	-0.436	-0.276
P3	0.492	0.234

[a] The orthogonal coordinate system (X,Y,Z) corresponds to the crystal abc axes.

It should be noted that the orange form is metastable and converts to the red form on prolonged reflux during the preparation. The methods of preparation of the two forms differ only in the nature of the excess reagent (see Chapter II and references therein). The red form is prepared by slow addition of triphenylphosphine to 'rhodium trichloride' i.e. the rhodium trichloride is normally in excess, whereas the orange form is prepared such that triphenylphosphine is the excess reagent. The difference is then kinetic and suggests that the immediate precursors to the forms of $RhCl(P(C_6H_5)_3)_3$ are different and dependent on the reaction conditions. In the orange form the product is not produced in its ground state. It could thus be temporarily locked [119] in the metastable geometry by the particular arrangement of the triphenylphosphine groups.

The rhodium-ligand distances (uncorrected for thermal motion) of this study, the equivalent values reported by Mason *et al.*,[138,140] and the relevant data on RhLCl are compared in Table 46.

The two determinations of the red form are in excellent agreement and no significant deviations can be detected. For the red form the rhodium-phosphorus bond lengths to the chemically equivalent phosphorus atoms

Table 46

Distances (in Å) from Structures Containing the $RhCl_2P_3$ Fragment

	$RhCl_2P_3$'[a] (red)	$RhCl_2P_3$'[a] (red)[c]	(orange)	RhLCl
Rh-Cl	2.376(4)	2.386	2.404(4)	2.381(2)
Rh-P (P *trans* to Cl)	2.214(4)	2.210	2.225(4)	2.201(2)
Rh-P	2.322(4)	2.320	2.304(4)	2.288(2)
(P *trans* to P)	2.334(4)	2.331	2.338(4)	2.288(2)[b]
ΣRh-ligand	9.246	9.244	9.271	9.158
ΣRh-P	6.870	6.861	6.867	6.777
	this work	(138,140)	Chap. V	(140)

[a] P' represents triphenylphosphine

[b] related by symmetry to the value above

[c] most recent values for this work are available as a private communication in ref. 140

(P1 and P3) are the same within experimental error in contrast to an apparently significant difference in the orange form. In all four structure determinations the chemically unique rhodium-phosphorus bond is substantially shorter than the other two. As mentioned in

Chapter V this extreme shortening may be attributed to significant π-acidity of triphenylphosphine. The complex RhLCℓ shows considerably shorter rhodium-phosphorus distances than $RhCℓ(P(C_6H_5)_3)_3$.

In $RhCℓ(P(C_6H_5)_3)_3$, (red form), the rhodium atom has one particularly close contact [142] with an *ortho* hydrogen of the 11 phenyl group. This contact (Rh-H112, 2.77 Å) is apparently caused by repulsions involving atoms on the opposite side of the phenyl group (Table 43). No attractive character is attached to this contact. It should be noted that the short contacts in the orange form and RhLCℓ involve phenyls attached to the chemically unique phosphorus and correspond to H216 in Fig. 14.

There appears to be a significant difference ($\Delta/\sigma \sim 4$) between the rhodium-chlorine bond lengths observed in the red (2.376(4) Å) and the orange (2.404(4) Å) forms. This difference persists even when the bond lengths are modified for the effects of thermal motion. This variation could be the result of the greater inter-ligand repulsions which are present in the orange crystals and it is reasonable that the effect should be noticeable in the weaker rhodium-chlorine bond rather than the rhodium-phosphorus bonds. Although the rhodium-phosphorus and rhodium-chlorine bond lengths support this view the difference may simply be an artifact of the data and thus not significant.

The geometry of the triphenylphosphine ligands is normal with respect to the angles C-P-C and Rh-P-C (Table 42): C-P-C, free ligand ~ 103°; [129] complexed ligand ~ 102°; Rh-P-C ~ 115°. However the geometry is abnormal with respect to the phosphorus-carbon distances. The average of the six-phosphorus-carbon distances involving P1 and P3 is 1.835 Å whereas the other three distances involving P2 average 1.850 Å cf. 1.828 Å for the free ligand. No comparable trend is reported in RhLCℓ. In fact in this molecule there is no apparent difference between P-C (sp^2) and P-C (sp^3) which has been observed in other phosphine complexes where the phosphorus is attached to aryl or alkyl substituents [143]. The comparable values for the orange form were 1.838 Å and 1.855 Å respectively. Combining the data from the two modifications gives mean phosphorus-carbon bond lengths of 1.837(4) Å and 1.852(5) Å for the two types of triphenylphosphine ligands. By normal crystallographic standards the phosphorus-carbon bonds of the phosphine *trans* to the chlorine atom are significantly larger than normal (Δ/σ ~ 4) while no convincing difference is observed between the phosphorus-carbon distances of the mutually *trans* phosphines, typical literature values [17,18,129] and the average phosphorus-carbon bond distance (1.827(9) Å)

observed in the dioxygen derivatives as mentioned in Chapters III and IV.

It would be pleasing if the extremely short rhodium-phosphorus bond, the lengthening of the associated phosphorus-carbon bonds and π-bonding could be related in a simple manner. Arguments using covalent radii for spherical atoms, to explain metal-phosphorus distances are tenuous since the geometry about the phosphorus atom is far from tetrahedral [143] and an anisotropy of covalent radius is expected as a result of the different mixtures of 's' and 'p' character in the various bonds [144]. Since the 3s and 3p orbitals have distinctly different radii [145] then σ-bonding alone would predict short metal-phosphorus and long phosphorus-carbon bond lengths when compared to values based on a simple covalent radius (r_{sp^3}) for phosphorus. As mentioned the angular properties of the coordinated triphenylphosphine are essentially the same as the free ligand so such a description cannot explain the phosphorus-carbon distance variation. The difference could be explained by greater participation of phosphorus 3d orbitals in the phosphorus-carbon σ-bonding, if the argument concerning the differences in radial properties of the phosphine atomic wave functions is extended to include these orbitals.

The π-acidity of phosphine ligands involves phosphorus 3d orbitals and the σ and π components of the bonding are not separable in this case, thus the 3d orbitals should also participate in σ-bonding. The lengthening of the phosphorus-carbon bonds should then be related to the extremely short rhodium-phosphorus bond and π-bonding.

While this explanation may look plausible certain conflicting evidence does exist particularly in the structure of RhLCℓ which should show very similar features to $RhCℓ(P(C_6H_5)_3)_3$ with differences due to the constraints of the tridentate phosphine ligand. As indicated previously the long phosphorus-carbon bonds do not exist in this structure. The explanation is then either incomplete or incorrect. The probability of an error of this magnitude and direction (0.02 Å too long) in any of the structures under consideration seems low. There is a difference in the nature of the inductive effects [146] of the substituents of the chemically unique phosphorus atoms in these structures. In $RhCℓ(P(C_6H_5)_3)_3$ the three substituents are electron withdrawing phenyl groups whereas there is only one electron withdrawing phenyl group and two electron donating aliphatic chains in RhLCℓ. Thus the observed phosphorus-carbon bond lengthening might be very specific to triarylphosphines in an extensive π-

bonding situation. Considerably more data are required to solve this problem.

Finally the structural trends of $RhCl(P_3')$ and its derivatives can be analysed. The molecules fall into two classifications: (a) coordinatively unsaturated - $RhCl(P_3')$, $RhCl(P_2'(CS)$, $RhCl(P_2'(C_2F_4)$, (b) coordinatively saturated - $(O_2)RhCl(P_3')$, $[(O_2)RhCl(P_2')]_2$. The trends corresponding to ligand replacement within each group can be analysed and then trends associated with ligand addition can be deduced. The three species present in group (a) contain a common structural fragment $RhCl(P_2')$ with the only differences being due to the ligand *trans* to the chlorine atom. The data for these complexes are summarised in Table 47. These data show a small range of rhodium-chlorine distances (the value 2.404(4) Å for the orange form of $RhCl(P(C_6H_5)_3)_3$ should probably be excluded from the comparison for reasons cited earlier). The significant changes in the rhodium-phosphorus bond lengths *cis* to the chlorine atom must then reflect changes in rhodium-phosphorus π-bonding [141] and the ligands can be arranged in order of π-acidity - C_2F_4 > CS > $P(C_6H_5)_3$.

Table 47

Ligand *trans* to Cl	Rh-Cl (Å)	Rh-P (*trans* to P) (Å)	Ref.
$P(C_6H_5)_3$(red)	2.376(4)	2.328 {2.334(3), 2.322(4)}	This work
$P(C_6H_5)_3$(red)	2.386	2.326 {2.320, 2.331}	138,140
$P(C_6H_5)_3$(orange)	2.404(4)	2.321 {2.304(4), 2.338(4)}	Chap. V
CS	2.386(3)	2.336 {2.335(2), 2.337(2)}	121
C_2F_4	2.375(8)	2.372 {2.374(8), 2.370(8)}	138

The group (b) compounds are compared in Table 48. The common structural fragment is $O_2RhClP'_3$. The geometry of these complexes can be treated as trigonal bipyramidal and the differences occur in an axial position. Within this series the rhodium-chlorine distances are effectively constant. The greatest changes occur in both the axial and equatorial rhodium-phosphorus distances. In the *tris*-phosphine complex these distances are longer by approximately 0.06 Å and 0.08 Å respectively. This difference must be mainly due to the different axial ligands P' and O2'. The oxygen in the axial position has no

Table 48

	$O_2RhCl(P'_3)$ Distance (Å)	$[O_2RhCl(P'_2)]_2$ Distance (Å)
equatorial		
Rh-Cl	2.391(3)	2.390(3)
Rh-P	2.357(3)	2.277(3)
$Rh-O_2$	2.043[a] (2.081(8), 2.005(8))	2.090[a] (2.198(7), 1.983(7))
axial		
Rh-P	2.375[a] (2.362(4), 2.387(4))	2.314(3)
5th other ligand	P'	O2'

a - average of two distances.

vacant orbitals in a suitable geometry to accept π-electrons from the rhodium. Thus in $O_2RhCl(P'_3)$ there are four ligands (3P' and O_2) competing for π-electron density whereas in the half unit of $[O_2RhCl(P'_2)]_2$ there are only three ligands (2P' and O_2) and it would be reasonable to expect the observed trend but not perhaps the magnitude. The average rhodium-oxygen distance is greater in the dimeric species than in the monomeric *tris*-phosphine

complex. However while the average is higher one distance is short (1.983(7) Å) and the other very long (2.198(7) Å). While it is difficult to assess how much of this assymmetry is due to the nature of the bridge in the dimer the difference parallels the trend observed in $O_2RhC\ell P'_3$. In this latter case the rhodium-oxygen (O pseudo *trans* to P) distance was significantly longer than the rhodium-oxygen distance involving O pseudo *trans* to Cℓ. In the dimeric species the magnitude of the difference is much greater. In discussions of the '*trans*' effect it is convenient to view the molecules as having a distorted octahedral geometry (i.e. each oxygen occupies a separate site rather than O_2 occupying a single coordination site). If the '*trans*' effect is modified by the extent of π-bonding [139,141] and the difference in rhodium-phosphorus bond lengths ($O_2RhC\ell P'_3$ to $[O_2RhC\ell P'_2]_2$) reflects an increase in the π-bonding, then a more marked assymmetry for the bound dioxygen in $[O_2RhC\ell P'_2]_2$ would be expected regardless of the constraints due to bridge formation.

The changes in geometry that accompany the chemical reaction:

$$RhC\ell P'_3 + O_2 \rightarrow O_2RhC\ell P'_3$$

can be summarised as follows:

(1) An oxygen molecule can be expected to approach an open site of $RhCl(P'_3)$ to form a square pyramidal intermediate which transforms to a trigonal bipyramidal structure by normal angular deformation. This is supported by the only major angular changes upon oxygenation being within the equatorial plane ligands (see Tables 12, 22, 32, and 42).

(2) The rhodium-phosphorus bond lengths increase.

(3) No change in rhodium-chlorine distances.

The constancy of the rhodium-chlorine distances throughout the series and the variation in rhodium-phosphorus bond lengths supports the concepts of π-bonding for the ligands P' and O_2. Electro neutrality for the rhodium atom is then achieved by variations in the π-bonding components.

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Appendix 1

Programmes Used

Author	Title	Description
D.P. Shoemaker	MIXG2	Calculates Picker diffractometer settings
M.J. Bennett	PMMO	Calculates intensities, makes LP corrections for Picker data
M. Elder	D-refine	Refines axial lengths (modified by K. Simpson)
A. Zalkin	FORDAP	Fourier summation for Patterson or electron density maps
M.J. Bennett	MMMR	Calculates starting parameters for rigid bodies or hindered rotors.
W.C. Hamilton	GONO9	Absorption correction calculator
C.T. Prewitt	BURP	Enlarged version of SFLS5HR structure factor calculation and least squares refinement (modified by B. Foxman and W. Brooks)
G.J. Williams	CROMERS	Calculates form factors curves from Cromer's coefficients
J.S. Wood	MGEOM	Calculates bond lengths, angles and best planes

W. Busing and H.A. Levy	ORFFE II	Calculates bond lengths, angles and associated errors (modified by B. Penfold, W.L. Brooks and M. Elder)
C. Johnson	ORTEP	Writes plot command tape for Calcomp plotter
M. Cowie	PUBE	Sorts reflection data according to any desired hkℓ sequence
R.C. Elder	PUBTAB	Tabulates reflection data for publication (modified by M. Cowie)

All programmes were run using an IBM 360 model 67 computer.

Appendix 2

Conventional Crystallographic Symbols as Defined in Vol. I, Page xi, of the International Tables for X-ray Crystallography

h,k,ℓ	indices of the reflection from a set of parallel planes
a,b,c	lengths of unit cell edges
α,β,γ	interaxial angles
a^*, b^*, c^*	lengths of reciprocal unit cell edges
$\alpha^*, \beta^*, \gamma^*$	interaxial angles in reciprocal space
$x_i, y_i, z_i,$	fractional coordinates of an atom i in units of a,b,c
$F_{hk\ell}$	structure factor for the unit cell, corresponding to the Bragg reflection $hk\ell$.
$\bar{u}^2$	mean square amplitude of atomic vibration
B	Debye isotropic thermal parameter; $B = 8\pi^2\bar{u}^2$
$U_{11}, U_{22}, U_{33},$	anisotropic thermal parameters used to describe ellipsoidal electron distribution of the anisotropically vibrating atom; the temperature factor expression is then: $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}b^2B^{*2} + U_{33}\ell^2c^{*2} + 2U_{12}hka^*b^* \cos\gamma^* + 2U_{13}h\ell a^*c^*\cos\beta^* + 2U_{23}k\ell b^*c^* \cos\alpha^*)]$
F_o	observed structure factors
F_c	calculated structure factors